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CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.[1]

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THE mineral cerite was first found in one of the iron mines of Bastnäs, in Westmanland, Sweden. Its peculiarity was noticed as early as 1751 by Cronstedt,[2] and in 1784 it was analyzed by d'Elhuyar,[3] in Bergmann's laboratory, and was considered by these two chemists to be a silicate of lime and iron. In 1803 the mineral was again examined by Berzelius and Hisinger, and by Klaproth, and nearly at the same time, but independently, they discovered in the mineral a new oxide. Berzelius and Hisinger named the earth *ceria*,[4] after the planet Ceres which had been discovered two years before by Piazzi. Klaproth called it *ochroiterde*,[5] from its brownish-yellow color. Fortunately the former name was adopted, for the latter name would have been a misnomer, since pure cerium dioxide, as we now know it, has a pale-yellow color.

From that time to the present, cerium and its compounds have frequently been the subject of investigation, but the work of the earlier chemists is not of direct importance, since the ceria upon which they worked was, as we now know, a mixture of various oxides, chief among them being those of cerium, lanthanum, and didymium.

In 1839, however, Mosander make known a discovery of the highest importance; namely, that ceria was not a simple oxide

[1] Read at the Brooklyn Meeting, August 15, 1894.
[2] *Sv. Vet. Akad. Handl., 1751*, S. 227.
[3] *Sv. Vet. Akad. Handl., 1784*, S. 121.
[4] *Afhandl. i. Fysik, Kemi och Mineral.*, 1, 58.
[5] *A. Gehl.*, 2, 303; *Beiträge*, 4, 140.

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but a mixture of at least two. The newly isolated earth he called *lanthana*, and this, in 1842, he split up into lanthana proper, and another oxide which he named *didymia*.[1]

Dating from the time of Mosander's discoveries, the results of the various investigations upon cerium acquire, of course, much greater value, but the chemistry of this element and the other rare earths has remained one of the most difficult problems in the field of inorganic chemistry, chiefly because of the great similarity in the chemical behavior of these different elements and the consequent difficulty of separating any one of them completely from the others. Naturally, then, in an experimental investigation of the compounds of cerium, the first problem to be solved is the preparation of pure ceria.

I. SEPARATION OF CERIA FROM THE OTHER EARTHS.

The ceria was extracted from allanite from Amelia County, Virginia, a large amount of this mineral having been most kindly sent to us by Professor W. G. Brown, of the Washington and Lee University.

Nineteen hundred and twenty-four grams of the finely powdered allanite was heated in large porcelain evaporators with concentrated hydrochloric acid until the supernatant liquid became dark brown. The syrupy liquid was allowed to cool and was then poured off, the residual mineral being again treated in the same manner until it became grayish-white, three treatments of about ten hours each usually sufficing. A portion of the residue was then moistened with concentrated sulphuric acid and heated until all of the acid was driven off. The white residue was thrown, in small portions at a time, into ice-water, and to the filtered solution, oxalic acid was added. No precipitate resulted showing that the treatment with hydrochloric acid had removed all of the rare earths.

The rare earth chlorides, mixed with those of iron, aluminum, calcium, etc., were then diluted and filtered. A portion of this filtrate was treated with hydrogen sulphide for twenty-four hours, the solution being kept at 70°, but no precipitate appeared. The hydrogen sulphide was then expelled by boiling, the sulphur was filtered off, and the filtrate was added to

[1] *Förh. Skand. Naturf. Stockholm, 1842*, 387; *Phil. Mag.*, **28**, 241; *Pogg. Ann.*, **56**, 503; *J. prakt. Chem.*, **30**, 276.

the original solution. This was oxidized by nitric acid and a concentrated solution of oxalic acid was then added in excess. The pinkish-white precipitate of the rare earth oxalates was allowed to settle, and the oxalates were then washed by decantation with hot water until the supernatant liquid was colorless. They were then digested in large evaporators with one per cent. hydrochloric acid until all iron had been removed and were then dried and ignited in a muffle furnace. The reddish-brown oxides resulting weighed 410 grams, a yield of over twenty-one per cent.

The oxides were dissolved in concentrated nitric acid. To facilitate solution sulphurous acid was added to one portion and oxalic acid to another, but with no perceptible benefit in either case. There were obtained four liters of an almost syrupy solution which showed the didymium absorption bands very strongly.

Many different methods for separating the ceria from the accompanying earths have been proposed but none of them seem to yield cerium which is completely free from lanthanum and didymium unless the method proposed be many times repeated. Mosander,[1] the earliest worker upon this problem, obtained a mixture of didymia and lanthana free from ceria by precipitating the mixed chlorides with potassium or sodium hydroxide and passing chlorine through the suspended hydroxides. Cerous hydroxide is oxidized to the insoluble ceric hydroxide while the hydroxides of lanthanum and didymium are changed to chlorides and dissolve. Jolin[2] found that the treatment must be made seven times before the ceria is completely free from didymia and lanthana. Popp[3] added sodium acetate to the solution of the chlorides and ran in chlorine, the cerium being precipitated. Later instead of passing in chlorine gas he added sodium hypochlorite and boiled. Gibbs[4] boiled the mixed earths with nitric acid (1:2) having first added considerable lead dioxide. Zschiesche[5] heated the rare earth sulphates with red lead and nitric acid. In each of the last two methods ceric oxide is formed. Winkler[6] separated ceria and didymia from lanthana by adding

1 *Phil. Mag.*, **28**, 241.
2 *Bihang till K. Sv. Vet. Akad. Handl.*, **2**, 14; *Bull. Soc. Chim.*, [2] **21**, 533.
3 *Ann.*, **131**, 359; *J. B.*, *1864*, 195 and 702.
4 *Sill. Amer. Jour.*, [2] **37**, 332.
5 *J. prakt. Chem.*, **107**, 65.
6 *J. prakt. Chem.*, **95**, 410.

mercurous oxide to the solution of the chlorides and then potassium permanganate until the solution is colored by the latter. Ceria and didymia are precipitated. Welsbach[1] precipitates the ceria by fractional crystallization as cerium ammonium nitrate. Bunsen first[2] proposed to ignite the oxides with magnesia, to dissolve out the ceria as cerium magnesium nitrate and then pour the solution of the latter into a large amount of very dilute nitric acid, whereby ceric oxide is precipitated. Later[3] he abandoned this method and proposed instead the method which has been most employed for preparing pure ceria. A solution of impure cerium sulphate is poured into boiling water containing one part of nitric acid to the thousand, and basic cerium sulphate is thrown down. This procedure must be repeated several times and is also very wasteful because the yield is small, so that it can be used with advantage only on material that is already nearly pure. Brauner[4] increased the yield by dissolving finally in nitric acid instead of in sulphuric acid, driving off the excess of acid and precipitating with boiling water containing nitric acid. Debray[5] fused the nitrates of the earths with from eight to ten times their weight of potassium nitrate at a temperature between 300° and 350°. The nitrate of cerium is decomposed leaving the oxide which is insoluble in water. The other nitrates are undecomposed and are soluble in water. Many repetitions were necessary to free the ceria from the other earths. Pattinson and Clark[6] heated the mixed chromates to 110° when cerium chromate decomposes to ceric oxide, the other chromates remaining unchanged.

For the separation of the ceria from the other earths in the allanite solution obtained as stated above, the authors first employed the Mosander-Jolin method which so eminent an investigator as Cleve has pronounced to be the best. The nitrate solution of the earths was diluted, potassium hydroxide was added in excess and well-washed chlorine gas was run into the solution for from four to five days. The white precipitate of

1 *Monatsh. f. chem.*, **4**, 630.
2 *Ann.*, **105**, 40.
3 *Pogg. Ann.*, **155**, 375.
4 *Monatsh. f. chem.*, **6**, 792.
5 *Compt. rend.*, **96**, 828.
6 *Chem. News*, **16**, 259.

the hydroxides soon changed to a dirty violet and became light yellow soon after the action of the chlorine began. The ceric oxide was washed by decantation until the wash-water gave no precipitate with ammonium hydroxide, this washing occupying nearly a week as the precipitate settles very slowly. The precipitate was then dissolved in hydrochloric acid and the treatment with chlorine was repeated. After seven complete treatments the concentrated solution of cerium chloride showed no absorption bands when a layer ten cm. thick was examined with a Krüss spectroscope. The solution was then nearly neutralized with ammonium hydroxide and hydrogen sulphide was run in for twenty-four hours, the solution being warmed to 70°. A very slight precipitate of copper sulphide resulted. This was filtered off, the hydrogen sulphide was expelled by boiling and the separated sulphur was removed by filtration. To the filtrate was added a concentrated solution of pure oxalic acid, a snow-white precipitate of the oxalates of the rare earths resulting. This precipitate was treated with a hot solution of hydrochloric acid (two per cent.) until the washing liquid failed to give a reaction for iron when tested with potassium sulphocyanate and ether. The oxalate was then dried and ignited in porcelain crucibles over the blast-lamp. The resulting oxide was of a pale yellow color resembling in tint very light chamois leather.

In the meantime the method of separation proposed by Debray was tried upon another portion of the rare earths. It was found that the melting point of the mixture of rare earth nitrates and potassium nitrate was usually about 325°. (The melting point of potassium nitrate is stated to be 339°.) Upon treating the fused mass with water it was found that the insoluble residue contained, even after two fusions, appreciable amounts of didymium. Since cerium nitrate begins to decompose at 200° and didymium nitrate at about 300°, the cause of the presence of didymium in the insoluble cerium oxide is evidently to be ascribed to the high melting point of the nitrate mixture employed by Debray. If then the melting point of the mixture could be lowered the probable result would be that less of the didymium nitrate would be decomposed and it seemed reasonable to expect that, by sufficiently depressing the melting point,

cerium oxide completely free from didymium might be obtained by a single fusion. With this end in view the potassium nitrate was replaced by sodium nitrate, the melting point of the latter, 316°, being somewhat lower than that of the potassium nitrate. But even with this salt more than two fusions were necessary to free the cerium from didymium.

Carnelley and Thomson[1] have shown that while potassium nitrate melts at 339° and sodium nitrate at 316°, a mixture of these two salts in molecular proportion melts at 231°. Consequently, this mixture was next tried with the rare earth nitrates, the details of the method being as follows:

The oxalates of the rare earths, after being freed from iron, as above described, are placed in porcelain evaporating dishes, the oxalates being covered by funnels of such size that when inverted they fit inside the edge of the evaporating dish. Concentrated nitric acid is now poured over the oxalates. Action begins at once in the cold, but it can be greatly hastened by warming on a water-bath. After the nitrogen oxides cease to come off, and the liquid has become clear, the solution, which should be so concentrated as to be syurpy in consistency, is poured while still hot into large porcelain crucibles half-filled with the well-ground mixture of potassium and sodium nitrates. About enough of the solution to completely cover the dry nitrates is poured in and the whole is thoroughly mixed by stirring.

For heating the crucibles a double air-bath was used. Both of the air-baths and the two covers were lined within and without with asbestos board. Through the two covers, openings were made through which thermometers could be introduced at various points within the inner bath. The crucibles were placed in circular openings cut in a piece of asbestos board, this board resting on pipe clay rods in the inner air-baths. The asbestos board was also pierced with many smaller openings to allow free circulation of air. The air-bath was heated by two Bunsen burners, the height of the flame being kept constant by means of "precision" gas-cocks.

After the crucibles have been placed in position the temperature is brought up slowly, too rapid heating being liable to cause

[1] *J. Chem. Soc.*, 53, 782.

the mass in the crucibles to swell and run over the edge. The two covers are placed in position, and a thermometer is inserted through the center opening to such a distance that its bulb is on a level with the bottoms of the crucibles. The heat is gradually increased until the thermometer shows a temperature of 300° in the inner bath. The mixture melts at a little below 230°, and decomposition of the cerium nitrate begins almost immediately. As the temperature rises the brown fumes come off copiously, the evolution gradually lessening as the heating continues. If, after removing the covers, it is seen that the evolution of gas from the fusion has entirely ceased, then the decomposition possible at the temperature employed is complete. This usually takes from four to five hours after the temperature has risen to 300°. It was found that the cerium nitrate is not entirely decomposed even when the temperature has been kept at 350° for some time, and also that if the temperature rises above 320° the cerium oxide will contain some didymium. After the evolution of nitrogen oxides ceases, the bath is allowed to cool rapidly since by so doing the solid mass can usually be removed by inverting the crucible and tapping the edge gently. If it cannot be removed in this way it can usually be loosened by throwing a jet of hot water around the upper edge. The removal of the mass in a solid block is of advantage since the condition of the decomposition may be judged by the color of the oxide which has collected at the bottom. If it is bright yellow or nearly white the ceria is probably pure, but if brownish in color then some of the didymium nitrate also has been decomposed.

The solid mass is now treated with hot water which dissolves all but the oxides. These are allowed to settle and the supernatant liquid is decanted off through a filter. More hot water containing from four to five per cent. of nitric acid is poured over the oxides and the liquid is brought to boiling and poured while hot through the filter. This is repeated six times and finally the oxides are washed with hot water alone, the washing being continued until the wash-water gives no precipitate with ammonia.

The oxides are dissolved by heating them with concentrated sulphuric acid until fumes of sulphur trioxide begin to escape,

allowing the mass to cool and then treating it with a large amount of water. More rapid solution can, however, be effected by throwing a jet of water upon the hot sulphates and stirring the mass constantly. There is some tendency to spatter, but solution is obtained in much less time and with much less water than in the first procedure. A concentrated solution of cerium sulphate thus obtained showed no didymium absorption bands in a layer thirty cm. thick.

To test the separation quantitatively, weighed amounts of pure cerium and didymium oxalates were mixed, the mixture was dissolved in nitric acid as above described and the mass was fused with the mixed alkali nitrates. The soluble portion from the first fusion was evaporated down and again fused with the alkaline nitrates, and this solution and fusion was repeated in all four times. The temperature during each fusion was about 300°. The insoluble cerium oxide resulting from the fusions was in each case free from didymium, and of the total cerium taken more than sixty-three per cent. was obtained completely free from didymium by the four fusions.

Another sample of the mixed nitrates was fused at about 350°. The layer of cerium oxide which collected at the bottom of the fused mass showed a brown coloration at the edges, and the insoluble residue after being carefully washed and dissolved in sulphuric acid gave the didymium bands clearly. The filtrate tested by the hydrogen peroxide method mentioned below showed some cerium still present with the didymium.

From the foregoing it will be seen that while the method is not quantitative it is nevertheless quite rapid and the yield is comparatively high. Its chief merit lies in the fact that the cerium oxide resulting from each single fusion is free from didymium, an advantage which does not seem to be possessed by the other separation methods with which the authors are acquainted.

II. QUALITATIVE TESTS FOR CERIUM.

Early in the work the necessity arose for testing various solutions and residues for the presence of traces of cerium, and a comparison of the different methods which have been proposed was made to ascertain which test was most distinctive and delicate.

Until 1864, when Gibbs[1] proposed his lead dioxide test for ceria, no satisfactory method for the qualitative detection of this earth was known. In 1882, Hartley[2] proposed a more delicate and also a more easily applied test, using ammonium acetate and hydrogen peroxide. In 1885, Lecoq de Boisbaudran,[3] and also Cleve,[4] observed that hydrogen peroxide gave to solutions of cerium salts, to which an excess of ammonium hydroxide had been added, a precipitate of the same color as that yielded by Hartley's reagents; namely, an orange-red. Sonnenschein,[5] in 1870, had proposed the use of ceria as a test for strychnia, and Plugge[6], in 1891, has reversed this, using strychnia as a test for ceria. Finally, Gibbs[7], in 1894, has proposed to substitute bismuth tetroxide for lead dioxide in his test.

Hartley appears to have been the only observer previous to Plugge to test the delicacy of the reactions proposed. He found that if a quantity of a cerium salt, equivalent to one mgm. of the element, were dissolved in 100 cc. of water, the addition of ammonium acetate and hydrogen peroxide gave a distinctly brown or orange-red precipitate which could be filtered off, dried, ignited, and weighed. "Hence, we can separate one part of cerium from 100,000 parts of liquid."

To test the delicacy of these various reactions one-half gram of ceric oxide was dissolved, as sulphate, in a liter of water. Each cubic centimeter of this solution would contain one-half mgm. of ceric oxide. When one cc. of this solution was diluted to 100 cc., and five cc. of the diluted solution was boiled with excess of lead dioxide and nitric acid (1:2), a faint yellow tint was to be observed, but four cc. failed to yield a distinguishable color; that is, 0.025 mgm. can be detected in about seven or eight cc. The bismuth tetroxide detected 0.017 mgm. under the same conditions.

In testing Hartley's reaction, one cc. containing one-half mgm. was diluted to 100 cc., each cubic centimeter then containing

[1] *Am. J. Sci.*, [2] 37, 352.
[2] *J. Chem. Soc.*, 41, 202.
[3] *Compt. rend.*, 100, 605.
[4] *Bull. Soc. chim.*, [2] 43, 57.
[5] *Ber. d. chem. Ges.*, 3, 631.
[6] *Arch. d. Pharm.*, 229, 558.
[7] *Am. Chem. J.*, 15, 546.

0.005 mgm. of ceria. When two cc. of this solution was diluted so much that with the solution of ammonium acetate and hydrogen peroxide it formed about four cc., a yellow color was visible, especially on looking downward into the test-tube held above a white surface; 0.01 mgm. of ceric oxide, or rather the cerium salt equivalent to this, can, therefore, be detected. Ammonium hydroxide and hydrogen peroxide gave as distinct a color with one cc., that is, Boisbaudran's test is twice as delicate as Hartley's.

Next, Plugge's strychnia test was tried and proven to be as delicate as he claims. The strychnia solution is prepared by dissolving one part of strychnia in one thousand parts of sulphuric acid. The solution suspected of containing ceria, or a few cubic centimeters of it, is rendered alkaline by sodium hydroxide, evaporated to dryness, and a drop of the strychnia solution is added. One-tenth of a milligram of ceria gives a distinct blue or violet color changing to red. One-hundredth of a milligram gives a faint blue tinge which rapidly fades. If oxalic acid be present it must be decomposed or the test fails. Boisbaudran's test is then the most delicate of any yet proposed.

Finally, known amounts of lanthana and didymia (mixed) and ceria in solution were mixed and Boisbaudran's test applied. A distinct coloration of the hydroxides was produced when 0.01 mgm. of ceria was mixed with 0.1 gram of lanthana and didymia in about 100 cc. of solution.

To apply the test in the presence of a large excess of other rare earths, very dilute ammonium hydroxide solution should be employed and this added drop by drop until the first permanent hydroxide remains after shaking. The hydrogen peroxide is then to be added—only a couple of drops are needed—and the mixture well shaken. By this means the weakly basic ceria is precipitated almost alone and the orange-red color cannot be disguised.

III. CEROUS CHLORIDE.

The ceric oxide, prepared according to the directions given in the first section, was purified from any thoria present, by boiling the oxalate (prepared from the sulphate) with a concentrated solution of ammonium oxalate. Any thorium oxalate dissolved,

was poured off and a similar solution poured over the residual cerous oxalate. The whole was then bottled and allowed to stand for some months with occasional shaking. The mixture was then brought to boiling and the liquid again poured off, the residual oxalate being washed with a similar solution. This washed oxalate was then dissolved in nitric acid, care being taken to ensure full decomposition and it was then almost neutralized with ammonium hydroxide. Potassium hydronitride was then added[1] so long as it continued to throw down a precipitate. This was filtered off leaving a solution of cerium nitrate containing only potassium and ammonium salts with possibly traces of calcium. This solution was precipitated with ammonium hydroxide and washed by decantation until a liter of the wash-water left no residue on evaporation. The ceric hydroxide was then tested for calcium, potassium, etc., with the spectroscope and proved to be free from all foreign material. This pure hydroxide has been employed to prepare salts of cerium.

As this work has been in reality only preliminary to an extended study of cerium, many of the already known salts were prepared in order to become familiar with their characteristics, but of these there is no need to speak at length.

A salt, which may probably be rightly claimed to be a new compound, was prepared while endeavoring to obtain cerium tetrachloride. This latter should be capable of existence if cerium is properly placed in the periodic system. Every other element in group IV of that system forms such a chloride not even excepting lead.[2] Among other attempts made, one was as follows: A concentrated solution of cerous chloride, obtained by dissolving ceric chloride in hydrochloric acid and evaporating was placed in a wash-bottle surrounded by a freezing mixture (snow and salt) and dry chlorine gas run in. This was rapidly absorbed, and after a short time a white crystalline mass settled out. This was placed on a porous porcelain plate to remove the greater part of the liquid, and then the following experiments were tried with different portions.

An attempt was at first made to dry it to constant weight over

[1] Dennis and Kortright, *Am. Chem. J.*, **16**, 79.

[2] *Monatsh f. Chem.*, **14**, 505.

dry caustic potash in vacuo. A large, but irregular, loss of weight occurred and the crystals evidently effloresced. On exposing it to the open air again it gained in weight till almost as heavy as at first.

An attempt to dry it over calcium chloride gave a similar result. A portion was then dried in air, dust being excluded.

	Grams.
Weight of sample taken	2.9824
" " " after 72 hours	2.9801
" " " " 118 "	2.9790
" " " " 142 "	2.9786
" " " " 166 "	2.9786

The chloride therefore assumes a constant weight in air.

In analyzing this air-dried chloride the cerium was first precipitated from the aqueous solution of the salt by ammonium hydroxide. The precipitate was so gelatinous that it was difficult to wash it free from chlorides and the oxide obtained by ignition of the precipitate was not of a pure yellow color. The percentages of cerium obtained in two analyses were 38.01 and 38.19.

In two other samples the cerium was thrown down by ammonium hydroxide and hydrogen peroxide was added. The orange-colored hydroxide thus formed was not as gelatinous as that formed with ammonia alone, and was much more easily washed, but on ignition of the precipitate the resulting ceric oxide was of a pale pink color. This color may have been due to the presence of a small amount of a higher oxide, for the results—38.01 and 37.93 per cent. cerium—while not agreeing as well as could be wished, were too high (see analysis below). The chlorine was determined by precipitation as silver chloride and the water by the method suggested by Kraut.[1]

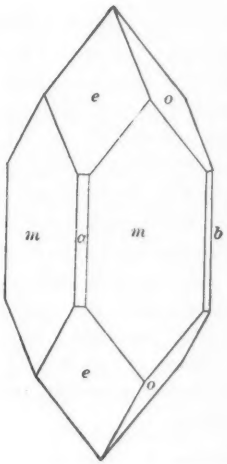
	Calculated for $CeCl_3 7H_2O$.	Found.
Ce	37.63	37.97
Cl	28.54	28.58
H_2O	33.83	33.88

The above analysis showed that the compound formed by passing chlorine into a cold saturated solution of cerous chloride was merely a finely crystalline form of cerous chloride and not a

[1] *Ztschr. anal. Chem.*, **2**, 242.

ceric chloride. Inasmuch then as the formation of the compound was probably due not to the oxidizing action of the chlorine, but to its dehydrating power, it seemed reasonable to expect that dry hydrochloric acid gas would accomplish the same result. The hydrochloric acid gas was made by the action of concentrated sulphuric acid upon solid ammonium chloride, the apparatus of Norblad being used for this purpose. Upon passing the gas into a cold concentrated solution of cerous chloride, the same white finely crystalline compound separated as with the chlorine. This was dried in the air to constant weight and then analyzed. In determining the cerium, the orange-colored hydroxide was precipitated by ammonium hydroxide and hydrogen peroxide but, before filtering, the solution was heated just to boiling. The suspended hydroxide changed to a bright yellow color but it did not become gelatinous and was easily washed. On ignition it yielded a ceric oxide of the usual pale yellow color.

	Calculated for $CeCl_3 7H_2O$.		Found.	
Ce.....	37.63		37.70	37.71
Cl	28.54		28.41	28.45
H_2O	33.83	by diff.	33.89	33.84



The crystalline form of the chloride was kindly determined by Mr. A. S. Eakle, of the Geological Department of the University, who states that "the cerous chloride is orthorhombic in crystallization, and of the form shown in the figure.

The axial ratio $\breve{a} : \bar{b} : c = 0.80834 : 1 : 1.44187$.

$a = \infty P \bar{\infty} (100)$
$b = \infty P \breve{\infty} (010)$
$e = P \bar{\infty} (101)$
$m = \infty P (110)$
$o = P \breve{\infty} (011)$

Faces.	Angles measured.	Angles calculated.
$110 : 1\bar{1}0$	$77^\circ 54'$	.....
$110 : \bar{1}10$	$102^\circ 12'$	$102^\circ 6'$
$101 : 011$	$49^\circ 20'$	....."

The above chloride seems to be distinct from that obtained by Jolin[1] and by Lange[2] for which the formula $2CeCl_3 15H_2O$ is generally given.[3] That chloride may be made by dissolving ceric hydroxide in hydrochloric acid and evaporating on the water-bath until the solution becomes quite viscous. This solution placed in a desiccator while hot solidifies on cooling to a crystalline mass of a yellow color. If these crystals be allowed to stand in the air, they lose their color and a glassy coating appears to form over the surface. The differences between the results obtained by Jolin and by Lange and the variation of each of their analyses from the calculated percentages made it seem desirable to repeat the analysis of chloride prepared by Jolin's method to see if better results could not be obtained. A sample of their chloride was therefore prepared by us and analyzed, but the results showed as great a variation from the theory as those already mentioned.

	Calculated for $2CeCl_3 15H_2O$.	Jolin.	Lange.	Magee.	Calculated for $CeCl_3 7H_2O$.
Ce	36.74	36.89	37.37	36.37	37.63
Cl.....	27.87	28.40	28.80	28.65	28.54
H_2O ...	35.39				33.83

IV. THE HYDROXIDES OF CERIUM.

The peculiar color changes of the hydroxides of cerium have often been noticed by chemists who have experimented with that element. When any one of the alkaline hydroxides is added to a solution of a cerous salt a white hydroxide is precipitated. This, so most authorities state, becomes slowly yellow on exposure to the air, more rapidly if chlorine or other oxidizing agents be present. Popp,[4] however, claims that he obtained a dirty violet hydroxide by leading chlorine into a solution of a cerium salt precipitated by an acetate. This he claimed to be a higher hydroxide than the yellow. He states that it gave on ignition a red oxide. Others have claimed that his violet hydroxide was a basic acetate. Rammelsberg[5] obtained a like-colored hydroxide by precipitating a hot solution of ceroso-ceric sulphate with caustic potash. Hermann[6] and Stapff[7] also obtained

[1] *Bull. Soc. Chim.*, [2] **21**, 153.
[2] *J. prakt. Chem.*, **82**, 129.
[3] *Gmelin-Kraut, Dammer and others.*
[4] *Ann.*, **131**, 361.
[5] *Pogg. Ann.*, **108**, 45.
[6] *J. prakt. Chem.*, **30**, 189; **92**, 113.
[7] *J. prakt. Chem.*, **79**. 257,

peculiar hydroxides to which they attempted without much success to assign formulas. Later Lecoq de Boisbaudran,[1] by the addition of ammonium hydroxide and hydrogen peroxide to a solution of a cerous salt, obtained an orange-red precipitate, which was studied by Cleve,[2] who, as a result of his observations, considered it the hydroxide corresponding to an unknown CeO_3; namely $Ce(OH)_6$.

The following observations may throw some light upon the matter. A solution of mixed chlorides, containing lanthanum, didymium, and cerium was boiled and precipitated, while hot, with ammonium hydroxide. This was done in a large bottle which could be tightly corked. The mixed hydroxides were almost perfectly white, having possibly a faint pinkish tint. After the hydroxides had settled, the supernatant liquid was poured off and the bottle was refilled with thoroughly boiled distilled water. This was repeated until all foreign salts had been removed, the bottle being kept closely stoppered except while decanting and refilling. The hydroxides suffered no change of color upon standing for some days. Therefore, cerous hydroxide and the hydroxides of didymium and lanthanum when mixed are almost white. Didymium hydroxide by itself, however, or without much intermixture of white hydroxides, has a pinkish color. Finally air was blown through the suspended hydroxides. The color rapidly changed, at first to a dull purple and finally to a pale yellow.

Next a solution of cerous chloride was treated in the same manner. The hydroxide remained perfectly white while air was excluded, but, being exposed to air, it took on a dull purple color changing later to a bright yellow. Through another similar sample, air freed from carbon dioxide was passed; the same change in color resulted. Through yet another, pure carbon dioxide was passed. It remained white and did not change to purple even when, after some time, air was substituted for the carbon dioxide, the stability doubtless being due to the complete transformation of the hydroxide to the carbonate. Through yet another sample, air from which both oxygen and carbon dioxide were removed, that is, nitrogen, was passed. It remained white. Next a bottle was about one-

[1] *Compt. rend.*, 100, 605. [2] *Bull. Soc. Chim.*, [2] 43, 57.

sixth filled with cerous chloride and this was precipitated—white—with ammonium hydroxide, and the bottle was then filled with unboiled water and lightly stoppered. The precipitate changed in color quite rapidly to light purple which gradually became darker from above downward and finally the top began to change to yellow. After about four months the upper third had become yellow, that below it being still violet.

Both the white and the purple hydroxides when washed on filter paper, dried at a low temperature and then ignited, gave an olive-green oxide, which did not become yellow even when the highest heat of the blast-lamp was applied. On powdering it very finely it seemed more nearly yellow. The weights seemed to agree well, however, with that called for by ceric oxide. The yellow hydroxide when dried and ignited gave a pale yellow ceric oxide. When the yellowish-white oxide prepared by this method or by igniting the oxalate is again ignited over the blast-lamp, but in an atmosphere of hydrogen, it becomes olive-green without marked loss of weight. For example 0.1263 gram of yellow oxide ignited in hydrogen weighed 0.1261 gram; 0.1574 gram similarly treated gave 0.1570 gram. When again ignited in air or oxygen, the oxide became yellow and regained its original weight. Bunsen[1] obtained very similar results.

As mentioned in a previous section, the precipitate obtained by the united action of ammonium hydroxide and hydrogen peroxide, on being dried and ignited, gives a pink oxide which seems to weigh somewhat more than ceric oxide, CeO_2, should.

Another point, perhaps worthy of notice, was that when some of the purple hydroxide was dissolved in sulphuric acid and allowed to stand for a few days there separated out a crystalline sulphate which, on analysis, gave results too high for cerous and too low for ceric sulphate.

It is to be concluded, then, so far as the present observations go, that cerous hydroxide is white; that on exposure to oxidizing agents including atmospheric air it becomes first purple and then yellow, or, in other words, the purple hydroxide is an intermediate product.

[1] *Ann.*, 105, 40.

CORNELL UNIVERSITY, July 7, 1894.

METHOD FOR THE DETERMINATION OF THE FREEZING-POINT OF FATTY ACIDS.[1]

By F. Wolfbauer.

Translated and Abridged by S. S. Emery.

BY reason of the lack of agreement between different chemists in the determination of the freezing-point of a fat, and also because of the commercial importance of this determination as indicating the quality of fats, it seemed desirable that a standard method for this determination should be adopted.

Accordingly, my proposed method, after being carefully examined by Dr. R. Benedikt, Dr. von Perger, Dr. Ferd. Ulzer, and myself, was agreed upon by us as the method by which all future determinations of the freezing-point should be made.

The method is as follows:

One hundred and twenty grams of the fat is melted in a beaker at a temperature but slightly above its melting-point, mixed with forty-five cc. of caustic potash solution (1,250 grams of caustic potash in one liter of water[2]), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with alcohol (fifty per cent.) to ascertain whether saponification is complete, indicated by obtaining a clear solution; otherwise it must be replaced in the bath and there allowed to remain until this is accomplished.

The soap is now decomposed by boiling with 165 cc. of dilute sulphuric acid (sp. gr. = 1.143 = 18° B.[3]), preferably done in a silver dish, and continued until the free fatty acid rises to the top as a perfectly clear oily layer.[4] The silver dish is then covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acid washed by boiling one-quarter of an hour

[1] From the Mittheilungen des Technologischen Gewerbmuseums, Wien, 1894.

[2] This solution should have a sp. gr. of 1.509, and contain forty-eight per cent. of potassium hydroxide.

[3] Or a mixture of twenty-two cc. concentrated sulphuric acid and 150 cc. water.

[4] If the size of the dish will permit of so doing, it is recommended to add (before decomposing) 150 cc. of boiling water, and allowing to stand ten minutes at 100° C.,—whereby the soap takes up water, rendering the subsequent decomposition more rapid

with dilute sulphuric acid (five cc. of concentrated sulphuric acid and 100 cc. of water). After settling and removing the dilute acid, it is boiled with 100 cc. of pure water,—this last being repeated should the washings taste distinctly acid. It is then dried in an open dish at 100° C. for two hours.

Only fatty acids obtained as above can be considered sufficiently pure and dry to be used for the determination of the freezing-point.

In the determination proper the following apparatus is employed: A thin-walled test-tube, three and one-half cm. by fifteen cm., is fixed by means of a cork in a suitable bottle A Centigrade thermometer, extending from 1° to 60°, and graduated in fifths of a degree, is fixed in the test-tube by a second cork, which must be sufficiently loose to permit of an easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28°. The amount of mercury *above* the surface of the fatty acid is thus diminished and a very appreciable error (a lowering of the freezing-point) is consequently avoided.

To accomplish the determination the test-tube is filled to within one cm., or one and one-half cm., of the top with the melted fatty acid, the thermometer immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about four cm. or five cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the thermometer is allowed to stand. The mercury now begins to rise in consequence of the latent heat liberated from the solidifying fatty acid; the highest temperature noted may be taken as the freezing-point.

The reading of the thermometer should be corrected for its inherent errors, previously determined. Its zero point should also be redetermined from time to time.

Each freezing-point determination should be repeated, and the difference between the two should not exceed 0.1° C.; as a rule it will not exceed 0.05°.

The use of narrower test-tubes than above prescribed, as well as lack of attention to other details, generally leads to low results, as a so-called "over-cooling" always appears in the passage from the liquid to the solid state.

The experiments which justified the adoption of this method were carried out in the following lines:

I. The influence of the method of saponifying.

II. The influence of the length of time of saponifying.

III. The influence of the degree of dryness of the fatty acid.

IV. The influence of the size and shape of the vessel in which the freezing-point is determined.

V. The influence of a different length of thermometer.

I. The Effect of the Method of Saponifying.—The following determinations show that either an aqueous or an alcoholic solution of caustic potash may be used for the saponification:

	Freezing-point found by means of	
	aqueous saponification.	alcoholic saponification.
Fatty acid I	43.00°	43.08°
Fatty acid II	43.49°	43.52°

It should be here remarked that, in the case of alcoholic saponification, a one and one-half hours' boiling of the soap solution diluted with one liter of water is necessary to completely remove the alcohol.

II. The Influence of the Length of Time of Saponifying.—The two following determinations were made on the same fat; in I the time of saponifying was limited to one and one-half hours, while in II it was prolonged to fully fifteen hours:

	Freezing-point.
Determination I	43.49°
Determination II	43.44°

It is therefore evident that a variation in the length of time of saponifying does not influence the final result.

Regarding the minimum length of time necessary, it varies with different fats,—slightly rancid fats requiring less than fresh fats, some of the former undergoing even spontaneous saponification on being mixed with the caustic potash. As a rule, however, for fresh fats two hours is amply sufficient, provided the fat was not melted at too high a temperature, and that, after

adding the caustic potash, a perfect emulsion was obtained by a vigorous stirring.

III. The Influence of the Degree of Dryness of the Fatty Acid.—Comparative tests have shown most conclusively that by increasing the amount of water in a fatty acid the freezing-point is lowered, and *vice versa*. Further, as the absorbent power of fatty acids for water is less in the cold than at a higher temperature, it follows that during the cooling of a fatty acid, saturated with the maximum amount of water, at a certain temperature a separation of water must take place, shown by the still liquid fatty acid becoming turbid. This turbidity naturally interferes with the detection of solidification, and consequently, determinations made on undried or partially dried fatty acids show much less agreement with each other than those made on the perfectly dried acid. In two determinations on the same fat, using the undried fatty acid, were obtained the

freezing-points	43.14°
and	42.86°
the freezing-points differing by	0.28°

If, after washing a fatty acid, a filtration be substituted for the drying, a partial removal of the water is thus effected. But as the freezing-point of a fatty acid so treated is 0.3°–0.4° lower than one similarly treated, but also dried, it appears that such a filtration is entirely superfluous.

As is shown in the following table, it makes no difference in the final result whether the fatty acid be dried only one and one-half hours or a much longer time. It is also immaterial whether the dried fatty acid be used immediately for the determination, or whether it be first allowed to solidify and to stand a long or short time, being subsequently remelted for the determination.

RESULTS OF A SERIES OF DETERMINATIONS OF THE FREEZING-POINT OF A FATTY ACID, BY AQUEOUS AND ALCOHOLIC SAPONIFICATION, AND USING THE DRIED FATTY ACID.

Determination. No	The saponification effected with	and continued.	Further treatment of the fatty acid.	Freezing-point found.	Difference from the average.
1.	Aqueous potash	15 hours	Dried 5 hours	44.44°	—0.02°
2.	" "	1½ "	" 4 "	43.49°	+0.03°
3.	A mixture of the above two dried fatty acids, washed again with water, filtered, and then dried two hours.			43.35°	—0.11°

4.	The fatty acid from the above test after standing twelve hours in the solid state, and then heated one hour.			43.51°	+0.05°
5.	Alcoholic potash...	½ hour.....	Filtered and dried one hour.	43.52°	+0.06°
6.	Aqueous " ...	3 hours....	Not filtered, dried two hours.	43.45°	−0.01°
7.	" " ...	The fatty acid from the above test after solidifying, immediately rinsed		43.46°	±0.00°
	Average			43.46°	

IV. The Influence of the Size and Shape of the Vessel in which the Freezing Point is Determined.—To ascertain what influence is exerted by the use of a narrower test-tube than prescribed, the freezing-point of two fatty acids was determined in a tube only two and one-half cm. in diameter, as well as in one of the usual diameter, three and one-half cm., with the following results:

	Freezing-point obtained in the wide tube.	in the narrow tube.	Difference.
Fatty acid I.....	43.52°	43.34°	0.18°
Fatty acid II....	42.88°	42.65°	0.23°
Average.....			0.20°

These results by no means fix the allowable minimum diameter of the tube, as, *a priori*, the possibility is not excluded of obtaining a still higher freezing-point by the use of a tube of still greater diameter.

Accordingly, the freezing-point of the same fatty acid was determined, first, in a test-tube of the usual diameter, three and one-half cm., and then in a similarly shaped vessel having a diameter of seven cm., making about four times as much fatty acid around the thermometer in the second case as in the first. The freezing-points obtained were as follows:

In tube three and one-half cm. in diameter..... 43.45°
" " seven cm. in diameter ..... 43.46°

which show that the diameter of the tube may be increased from three and one-half cm. without disturbing the ratio between the amount of heat radiating from the fatty acid through the walls of the tube and the amount of liberated latent heat.

Consequently a tube three and one-half cm. or more in diameter answers perfectly for the correct determination of the freez-

ing-point, but it is not permissible to use one appreciably narrower than this.

V. The Influence of the Length of the Thermometer.—In order to demonstrate and also to estimate the error (a too low result) caused by an incomplete immersion of the thermometer in the liquid, thus allowing a portion of the column of mercury to project above its surface, the shortened thermometer recommended above, and a long (normal) one were first tested by a complete immersion in a water-bath, when each registered exactly the same temperature (43°); after which they were simultaneously placed in the test-tube containing water at 43°. The shortened thermometer was immersed to the 35° mark, leaving but 8° of mercury above the surface of the water, while the long thermometer could be immersed to only its zero mark, leaving fully 43° of mercury exposed. The whole was then placed in an air-bath, kept at a temperature of 20° in order to avoid the error of radiation. The reading of the long thermometer was about 0.13° below that of the shorter one.

This error was now calculated for each thermometer, giving, theoretically, for the long

thermometer	0.15°
while for the shorter one, only	0.03°
the difference of	0.12°

being the theoretical error introduced by using a long (normal) thermometer, and agreeing closely with the experimental determination of the error (0.13°).

Though, of course, this error is not completely eliminated by using a shortened thermometer, still it is so reduced as to be of no practical importance.

RECENT WORK ON THE SUGARS.

By B. B. Ross.

(*Continued from page 553.*)

Received May 14, 1894.

DETERMINATION OF WATER IN SUGARS.

Herzfeld (*Ztschr. des Ver. f Rübenzucker*, **43**, 130, *Bull. Assoc. Chim. Belg.*, **6**, 267) reports the results of a large number of experiments in the determination of the amount of water in

syrups and sugars, the drying being effected both in air and in vacuo.

The drying in contact with air was conducted at a temperature of about 105° C., the samples under examination being contained in nickel dishes about eight cm. in diameter and two cm. deep.

For syrups, three grams of material were employed, along with thirty grams of well-purified quartz sand.

In the water determinations in vacuo, a temperature of about 107° C. was employed, while in the experiments with Soxhlet's drying apparatus, the operation was conducted at about 103°–104° C.

A syrup prepared by dissolving a definite weight of sugar in a known weight of water was used in a large number of the tests made.

After three hours drying in vacuo, the results secured closely approximated the theoretical figures, and at the end of five hours' drying the correspondence was almost exact.

In drying in air, eight hours were required to obtain results agreeing with the theoretical water content, and the loss in weight still continued, even after fifty-six hours' drying.

In the estimation of water in syrups, to which alkaline salts had been added, it was likewise found that concordant results could be most quickly secured in vacuo.

With raw sugars, as well as with syrups, the results by drying in air were quite appreciably higher than those secured in vacuo, especially where the drying was at all protracted.

For maintaining a temperature of approximately 105° C., the author employs toluene between the walls of the drying apparatus.

Josse (*Bull. Assoc. Chim. France*, **10**, 656) proposes to employ in the determination of water in syrups and masse cuite, a dried and weighed spiral of filter paper which is to be saturated with the sample under examination.

A strip of filter paper, one to two cm. wide and about three meters in length, is coiled into a spiral form, placed in a capsule about seven cm. wide and two cm. deep, dried and weighed.

Two grams of syrup or masse cuite is next brought into the dish, about six to eight cc. of water added, and after the mixture has been warmed slightly the paper spiral is inserted.

The liquid is readily absorbed by the filter paper, and the drying is conducted at 100°–110° C., until a constant weight is secured, about two hours being ordinarily required to complete the operation.

It is claimed that the method is accurate as well as rapid.

DETERMINATION OF ASH IN SUGARS.

Courtonne (*Bull. Assoc. Chim. France*, **10**, 223) describes in detail the method proposed by him for the determination of ash in sugars by ignition of the sample in the presence of ferric oxide. The process is conducted as follows:

Place in a platinum capsule two grams of freshly calcined ferric oxide, which should also have been thoroughly washed to insure freedom from sulphuric acid. Into the same vessel weigh five grams of sugar, or about two grams of molasses. After addition of a little water to the mass, the mixture is evaporated rapidly upon a sand-bath or a metallic plate and heated over a Bunsen burner until frothing takes place. The capsule is now placed in a muffle heated scarcely to dull redness; the combustion is found to take place quite rapidly, and the incineration is sometimes completed in a quarter of an hour—always within half an hour.

Among the advantages presented by this process, it is claimed that, as in the Alberti and Hempel method, where quartz sand is employed, the mass is well divided by the admixture with the ferric oxide, and the points of contact of the material with the air are thus multiplied. The formation of carbonates is also prevented and the ferric oxide facilitates oxidation by acting as a carrier of oxygen from the air to the sample; further, the low temperature employed prevents the loss of volatile salts, such as chlorides, while the rapidity of execution of the incineration is an important advantage.

This method should also have the preference over the quartz sand process for the reason that the platinum vessels used are much less readily attacked where ferric oxide is employed.

Vivien (*Bull. Assoc. Chim.*, **10**, 225) reports the result of experiments with Courtonne's method, employing different temperatures and different periods of time for the ignitions.

The results were found to be always lower than those secured

by the sulphuric acid method and the direct ignition process, the figures for the same sample not being at all concordant.

A constant weight was not obtainable by this process and the composition of the ash varied considerably with the length of time of the incineration and the temperature employed.

At somewhat elevated temperatures it was found that chlorides were more or less attacked and, possibly, partly volatilized.

ALBERTI AND HEMPEL'S METHOD FOR ASH DETERMINATIONS.

Stift (*Oest. Ztschr. Zucker*, **22,** 22; *Chem. Ztg. Rep.*, **17,** 102), as the result of a large number of experiments with different sugar products, concludes that this method, by proper and careful execution, and with previous thorough testing of the quartz sand employed, is to be most highly commended, yielding, as it does, concordant results and, in contrast to other methods, furnishing more correct and uniform figures for the content of inorganic substances.

A point of great importance in the performance of the incineration is the necessity of the employment of quartz sand of absolute and known purity.

With sugars containing considerable proportions of nitrates (which are decomposed in this process), it is necessary to make a separate estimation of nitric acid.

THE DETERMINATION OF VOLATILE AND INSOLUBLE FATTY ACIDS IN BUTTER FAT.

By W. H. Beal.

Received July 27, 1894.

A FEW years ago when called upon to make examinations of the fat in a number of samples of cream the author attempted to use for that purpose the then recently proposed method of Waller as modified by Moore[1] which is briefly as follows: Two and five-tenths grams of fat are placed in a weighed Erlenmeyer flask and saponified with one gram of potassium hydroxide dissolved in fifty cc. of seventy per cent. alcohol. After heating until saponification is complete the alcohol is driven off in a boiling water-bath. The resulting soap is dissolved in fifty cc.

[1] See *J. Am. Chem. Soc.*, 11, 144, *1889*.

of water and decomposed by means of twenty cc. of dilute sulphuric acid (one part of strong acid to ten parts of water). The flask is connected with a condenser and fifty cc. are distilled off, the distillate passing through a small filter in the mouth of the receiving flask. The distillate is titrated with one-tenth normal sodium hydroxide solution, using phenolphthalein as an indicator. Fifty cc. of water are added to the contents of the flask and an equal quantity distilled off and titrated as before. This treatment is repeated until only one-tenth cc. or less of soda solution is required to neutralize the distillate. After cooling, the liquid remaining in the flask is poured off from the solidified insoluble acids through the same filter used for the distillates. The insoluble acids are repeatedly washed with hot water until all traces of sulphuric acids are removed. The condenser is then washed out with hot alcohol and the filter exhausted with the same solvent, the washings being collected in the flask containing the insoluble acids. The alcohol is driven off and the flask and contents dried at 100° C. and weighed.

With proper precautions satisfactory results were obtained with this method, but the work had not proceeded far before grounds for the following objections became evident: (1) Saponification is slow and removal of the last traces of alcohol in the dilute solution recommended is difficult; (2) there is danger from violent bumping, which it was found impossible to entirely prevent; (3) there is danger of charring the fat adhering to the sides of the flask when the contents of the latter are reduced to a small bulk, causing the final insoluble acid to have a brownish color instead of a pale yellow color which is normal; and (4) inconvenience and loss of time is occasioned by the necessity of frequently replenishing the contents of the flask.

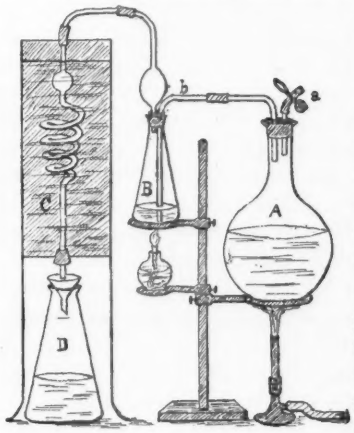
An attempt to devise a process which would in a measure, at least, overcome these difficulties, which it may be observed are in large part shared by all the methods now in vogue, resulted finally in the adoption of the following method of procedure:

Volatile Acids.—Two and eight-tenths to two and nine-tenths cc. (approximately two and five-tenths grams) of the pure fat were measured by means of a narrow pipette into a weighed Erlenmeyer flask (long narrow form preferable) of 200 cc.

capacity. Saponification was accomplished by adding two cc. of a solution prepared by dissolving fifty grams of potassium hydroxide (free from carbonates) in 100 cc. of water and five cc. of strong (ninety-five per cent.) alcohol. The flask was connected with a reflux condenser and heated on a water or steam-bath until saponification was complete. Five minutes was usually amply sufficient for this purpose. The last traces of alcohol were quickly and completely removed with the filter pump by means of a device described by L. F. Nilson.[1]

The soap thus obtained was dissolved in thirty cc. of warm water and decomposed with twenty cc. of a twenty per cent. solution of orthophosphoric acid. The volatile acids were expelled from the flask by means of a current of steam, using the apparatus described below. The operation was usually considered complete when 500 cc. had passed over, although, as an extra precaution, fifty cc. more was distilled over and titrated separately. For titration, decinormal soda solution and phenolphthalein were used.

The apparatus used in distilling is shown in the accompanying cut. A is a liter flask two-thirds full of water, which is kept boiling. The steam generated is forced into the decomposed soap solution in B through the tube b, which reaches nearly to the bottom of the flask. This second flask is provided with a small lamp, so regulated as to prevent increase, by condensation, of the solution in the flask, and finally to bring its contents to a small bulk (about fifteen cc.). The condenser C consists of a copper tank, fifteen inches high, twenty inches long, and five inches wide, having four perforations in the bottom, into which glass spirals are fitted by means of rubber stoppers, and provided with proper inlet and



[1] *Ztschr. anal. Chem.*, 28, 176.

overflow pipes for the water supply. Provision was thus made for four distillations at one time. The distillates were collected in wide-mouthed Erlenmeyer flasks, marked on the neck at 500 cc., and carrying funnels with small filters, through which the distillates passed.

Insoluble Acid.—After the distillation was completed, the condenser and connections were rinsed back with boiling water into the flask containing the non-volatile acids. The latter were shaken up with the hot water, and the solution, when cold, was passed through the same filter used for the distillate. Hot water (about 100 cc.) was again added, shaken up with the contents of the flask, and when cold filtered off as before. This operation was repeated until the washings contained no trace of phosphoric acid. The filter was then exhausted with hot, strong alcohol, and the solution allowed to run into the flask containing the insoluble acids. The alcohol was driven off on the water-bath and the fatty acids dried at 100° C. in the air-bath until they began to gain weight.

Very uniform and concordant results were obtained by this method in the examination of a large number of samples of butter fat.

The expulsion of the volatile acids by means of a current of steam, which it was afterwards found[1] had already been suggested by Goldman,[2] proved to be a decided improvement over direct boiling of the solution containing the fatty acids. When the operation had been started it required but little further attention and there was no danger of bumping or of overheating the insoluble acids. The volatile acids were very thoroughly removed, the last distillate of fifty cc. never requiring more than two-tenths cc. of soda solution for neutralization.

The first fifty cc. of distillate obtained by this method required less soda solution than that obtained by the Reichert or the Moore-Waller methods, and titration of each successive fifty cc. of the total 550 showed that expulsion of the volatile acids was much more gradual and uniform than in the latter methods.

1 *Analyst, Sept. 1892*, 174.

2 *Chem. Ztg., 1888*, **12**, 183; **14**, 216; and **20**, 317.

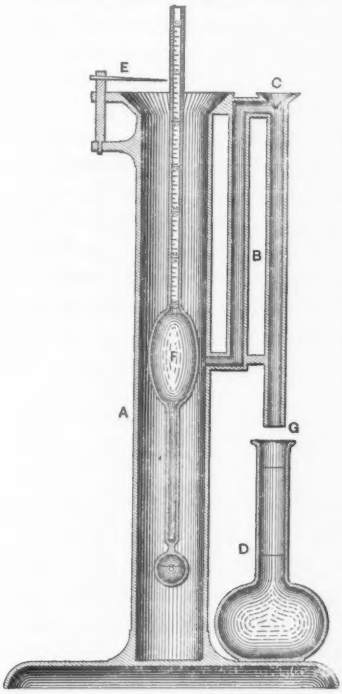
A GRAVIMETER FOR SUGAR ANALYSIS.[1]

By W. K. Gird.

Received June 28, 1894.

FOLLOWING is a description of the construction and operation of this apparatus; the drawing showing the instrument and appurtenances in section:

A represents the main tube to hold the solution under treatment; B, overflow pipe; C, air vent to prevent siphonage, constructed in funnel form to facilitate cleaning; D, the usual graduated flask; E is an index finger pointing to the saccharometer, constructed so as to swing out of the way when necessary, and to stand for convenience of reading, say five graduations above the surface of the fluid; F, hydrometer or saccharometer, weighing exactly 26.048 grams; G, point of discharge into the flask D.



Although the operation is manifest, a few explanatory words may be appropriate.

The operator closes aperture G with his finger, then fills the main tube with the solution until it shows full at C, then strike off foam from the top of the main tube, remove the finger from G and permit the excess to escape to the last drop which must be removed.

This will leave the tube B moistened with the fluid under analysis, so that the condition will be left precisely the same as it will be after the delivery of the discharge hereafter explained,

[1] Read before the Midwinter Fair Congress of Chemists at San Francisco, June 8, 1894.

so that there can be no loss nor no gain either in quantity or quality. Next, place flask D under the overflow G and insert the saccharometer in the usual manner bring up the mouth of the flask so as to catch the last drop. The fluid in the flask will then be the required quantity. Now bring the point E to the index on the saccharometer and note the reading for Brix, to which add five, representing the height of the finger above the surface.

This instrument is constructed upon the sole principle of displacement determined by the weight of the saccharometer which displacement is always the same, not being affected by difference of temperature, rendering the use of the thermometer and corresponding tables unnecessary.

In taking the Brix as described above, the precise weight is conveyed into flask D through the overflow, thus dispensing entirely with use of the pipette and weighing as in the old system.

The results are absolute, doing away with all liability to error, inasmuch as no readings are necessary and all the manipulations are regulated and controlled by easily observed limitations.

In making many analyses as for instance in the laboratory at Chino numbering perhaps 200 per day, the advantages derived from the use of this instrument both in rapidity and accuracy can scarcely be estimated.

NOTE.—This instrument has since been improved, notably in the addition of a permanently attached thermometer which, in addition to the usual thermal graduations, has also a table on its face for the corrections due to differences of temperature.

ON THE QUALITY OF POTASSIUM IODIDE, SOLD IN THE MARKET AS U. S. P.[1]

BY CHAS. O. CURTMAN.

Received August 4, 1894.

SIXTEEN samples were procured for examination by purchasing original packages made by twelve different firms. For six of them I am indebted to the courtesy of a friend, who bought them for a similar purpose and divided with me. To these, the tests of purity directed by the U. S. P. were applied seriatim, with the following results:

A. No residue should be left when one gram of the salt is dissolved in two cc. of diluted alcohol of sp. gr. 0.928. To this test fourteen specimens conformed; two left a small residue (Nos. 5 and 9).

[1] No. 5. Report Research Committee B.

B. To the test for excess of alkalinity the same fourteen specimens conformed, while two exceeded the limit (Nos. 5 and 9).

C. In the same two specimens and two others (5, 8, 9, 11), the flame test showed a considerable amount of sodium, while in the others the violet potassium flame appeared at once.

D. In both of these specimens (5 and 9) iodate was found (about 0.8 per cent.) while the others were free from it. (Nos. 5 and 9 were from the same firm.)

E. The hydrogen sulphide test showed the absence of metallic impurities in all of the sixteen specimens.

F. The barium chloride test indicated sulphate in five specimens (3, 5, 8, 13, 15); the others were free from it.

G. A small trace of nitrate was found, by reduction to ammonia, in three specimens (4, 7, 14); a somewhat larger amount in three others (3, 8, 13).

H. No iron could be detected in any of the specimens by potassium ferrocyanide.

I. Cyanide was absent in all specimens.

K. Titration with decinormal silver nitrate using potassium chromate as indicator, yielded with one gram each of the well-dried specimens as follows:

cc. of $\frac{N}{10}$ $AgNO_3$ required for one gram of specimen.	Per cent. of KI.	No. of specimens.
60.25	100.00	1, 10, 12
60.30	99.40	2
60.50	99.67	15
60.55	99.60	6
60.63	99.50	4, 7, 8, 11, 14

Making eleven specimens which conformed to the U. S. P. standard of at least 99.50 per cent.

60.70	99.40	5, 9
60.75	99.33	3
60.80	99.30	16
60.85	99.20	13

Making five specimens below standard.

(The second decimal of a cubic centimeter was estimated on graduation into one-twentieth cc., where it fell between 0.00 and 0.05). Bromide could not be detected in any of the specimens.

Chloride was found in eight specimens (Nos. 3, 4, 5, 7, 13, 14, 15, 16), by precipitating with a slight excess of silver nitrate, washing thoroughly, and digesting for about twenty-five

minutes in a five per cent. solution of ammonium carbonate (free from hydroxide). The filtered liquid became turbid on acidulation with nitric acid.

Mohr's method of titration with decinormal silver nitrate, using potassium chromate as indicator, gives direct results when bromide and chloride are absent and the impurity consists of substances which do not precipitate silver nitrate. But when chloride is present (bromide is very rarely found in potassium iodide), its smaller molecular weight will require the use of a greater volume of silver solution than would suffice for pure iodide, and a calculation becomes necessary to obtain correct values. This may be avoided by reference to the following table, which, for potassium iodide containing chloride as only impurity, gives the percentage of pure potassium iodide corresponding to the number of cubic centimeters of decinormal silver nitrate used for one gram of specimen.

cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.	cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.	cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.
60.2555	100.000	62.8	96.571	65.4	93.068
60.3	99.940	62.9	96.437	65.5	92.933
60.4	99.805	63.0	96.302	65.6	92.799
60.5	99.670	63.1	96.167	65.7	92.664
60.6	99.536	63.2	96.033	65.8	92.529
60.7	99.401	63.3	95.898	65.9	92.395
60.8	99.266	63.4	95.763	66.0	92.260
60.9	99.132	63.5	95.628	66.1	92.125
61.0	98.997	63.6	95.494	66.2	91.990
61.1	98.862	63.7	95.359	66.3	91.856
61.2	98.727	63.8	95.224	66.4	91.721
61.3	98.593	63.9	95.089	66.5	91.586
61.4	98.458	64.0	94.955	66.6	91.451
61.5	98.323	64.1	94.820	66.7	91.317
61.6	98.188	64.2	94.685	66.8	91.182
61.7	98.054	64.3	94.550	66.9	91.047
61.8	97.919	64.4	94.416	67.0	90.912
61.9	97.784	64.5	94.281	67.1	90.778
62.0	97.649	64.6	94.146	67.2	90.643
62.1	97.515	64.7	94.011	67.3	90.508
62.2	97.380	64.8	93.877	67.4	90.373
62.3	97.245	64.9	93.742	67.5	90.239
62.4	97.110	65.0	93.607	67.6	90.104
62.5	96.976	65.1	93.472	67.7	89.969
62.6	96.841	65.2	93.338	67.8	89.834
62.7	96.706	65.3	93.203	67.9	89.700

To avoid the error occasioned by potassium chloride, I repeated

some of the titrations with decinormal silver nitrate, using starch iodide as indicator (Pisani's method). A gravimetric method had been devised in 1872 at Goettingen, by Hübner, Spezia and Frerichs, in which thallous chloride was used as precipitant of iodides, and I concluded to convert this into a simple volumetric process and apply it to the present investigation. Thallous chloride, $TlCl = 239.07$, at 15° C., requires 360 parts of water for solution (100 cc. of water dissolve 0.2777 gram of thallous chloride). A centinormal solution requires 2.3907 grams of TlCl for one liter. Thallous iodide, $TlI = 330.23$, at 15° C. requires nearly 12,000 parts of pure water for solution, and about 16,000 parts if potassium chloride be present or still more if the water be acidulated with acetic acid. Thallous bromide is much more soluble than the iodide, and its solution precipitates iodide promptly.

After a trial of various substances as indicators of the final point, spotting with sodium palladious chloride was found to yield very accurate results. The titration was conducted as follows: 0.16556 gram of potassium iodide (ten cc. of a solution, containing 1.6556 grams in 100 cc.) were placed into a capacious flask and centinormal thallous chloride added until spotting showed the disappearance of iodide from the solution.

For spotting, a ten per cent. solution of sodium palladious chloride was, by means of a pipette drawn into a broad line (two mm.) upon a plate of milk glass (photographers opal) and permitted to dry. As soon as it became doubtful whether further addition of thallous chloride produced a precipitate, a drop of liquid was taken out of the flask with a glass rod and drawn across the line of palladious chloride upon the plate. As long as iodide was present a dark spot formed at the crossing, and the number of cubic centimeters used was marked at its end in pencil. At the opposite end of the palladium line a drop of a saturated solution of thallous iodide was placed, so as to serve with its faint color for comparison with the drops taken from the flask. To guard against deception the same specimen was repeatedly tested by different operators, but the indications corresponded sharply.

The following results were obtained, with the first six numbers

of the specimens by the three methods: Mohr's with silver nitrate and potassium chromate (one gram of the specimen being used and the percentage corresponding to the cubic centimeters inserted from the table). Pisani's method with silver nitrate and starch iodide (1.6556 grams being used and each cubic centimeter of $\frac{N}{10}$ $AgNO_3$ deemed equivalent to one per cent. of KI) and with the thallous chloride, (0.16556 gram being used and one cc. counted as one per cent.).

No. of specimen.	Mohr's method. cc. used.	Mohr's method. Per cent. KI.	Pisani's method. Per cent. KI.	Thallous chloride. Per cent. KI.
1	60.25	100.00	100.00	100.00
2	60.30	99.94	99.94	99.94
3	60.75	99.33	99.20	99.20
4	60.60	99.54	99.40	99.35
5	60.70	99.40	99.30	99.30
6	60.55	99.60	99.55	99.55

The method of Pisani and that with thallous chloride yielded somewhat less percentages with some of the specimens than Mohr's method, but gave, in almost every instance, results equal to each other.

SAINT LOUIS, MO., July 22, 1894.

SEWAGE DISPOSAL AT WORCESTER, MASS.

BY HARRISON P. EDDY.

Received February 6, 1894.

SINCE the description of the sewage disposal works at Worcester, by Dr. Leonard P. Kinnicutt, in 1891, (See *J. Anal. Appl. Chem.*, **5**, 544), many important changes have been made both in the methods employed and machinery used. The capacity of the plant has also been greatly increased. The amount of water then dealt with was 3,000,000 gallons per twenty-four hours, while now between 10,000,000 and 15,000,000 gallons are successfully treated in the same time.[1]

Before examining in detail the work accomplished it may be well to look briefly into the history connected with the purification of sewage at Worcester, that the problems encountered may be more fully understood.

For many years the city turned her sewage directly into the Blackstone river, a stream of about 23,000,000 gallons during

[1] Descriptions of this plant showing the engineering details are given in the *Engineering News* for January 11 and 18 and the *Engineering Record* for January 13, to which the reader is referred.

the summer months. This stream is fed, in part, by water from the northern water shed which tributary is called Millbrook, and it flows through the center of the city. This water amounts to about 8,000,000 gallons per day during the summer months. Millbrook being so conveniently situated was made the trunk sewer and to-day all the sewage of Worcester is discharged into it. For a number of years there was so little filth turned into the stream that the villages situated near the river, below the city, had little cause for complaint, but with the increase of population the river became very foul until, in 1886, the complaint from neighboring villages was heeded by the Massachusetts Legislature, and the right, granted in 1867, to turn sewage into the Blackstone river was revoked. An act was passed June 25, 1886, compelling Worcester to "remove from its sewage, before it is discharged into the Blackstone river, the offensive and polluting properties and substances therein, so that, after its discharge into said river * * * it shall not create a nuisance or endanger the public health." Four years were given the city in which to perfect some system for the accomplishment of this result, and accordingly, City Engineer Chas. A. Allen personally inspected works at home and abroad and after a careful study of the local problems recommended that a plant, capable of dealing with 4,500,000 gallons of sewage daily, be constructed and that the method of treatment employed be that of chemical precipitation.

This plant was first operated June 25, 1890, from which time until July, 1893, about 3,000,000 gallons of sewage were treated daily, except in time of storm when the entire flow was turned directly into the stream. It was found from the experiments of these three years that, by chemical precipitation, the sewage could be purified to an extent which would admit of its being turned into the river. Having settled this point, the next problem confronting the city was the treatment of the entire amount of sewage, as thus far only about twenty per cent. had been taken to the purification works. The actual amount of sewage is between 5,000,000 and 8,000,000 gallons per day, while the water from the brook, mentioned above, increases this to 10,000,000 or 15,000,000 gallons in dry weather, while in storm this amount is so largely increased that its treatment is wholly out

of question. The city is almost wholly sewered on the combined plan. From the start the plan had been to separate the waters of Millbrook from the sewage, thus leaving only a moderate amount of water with which to deal. On further consideration, however, it seemed advisable, for the present at least, to take as much of the sewage to the plant as possible. Accordingly, the present city engineer, then superintendent of the sewer department, Mr. F. A. McClure, proposed that ten additional settling basins, with the other necessary appliances, be provided, and that the whole, or as much as possible of the present flow be taken the to works. This plan having been adopted, work was begun in 1892 and the enlarged plant put in operation about the middle of July, 1893, since which time the entire flow has been treated.

The new basins differ somewhat from the old ones, being 166⅔ feet long and forty feet wide; the capacity is, however, the same, as are also the general features of construction. The effluent instead of returning to the steps provided in the old plant, is utilized to furnish power for pumping sludge during the day and for running a dynamo at night. A Shone ejector has been provided for pumping the sludge from the new work and part of that from the old. This ejector has proved to be very efficient and is much better adapted to use with sludge than the submerged centrifugal pumps employed on the original plant, as there is not the danger of clogging. It is run by air furnished by a compressor, power for which is derived from the water-wheel. Thus expense of steam is avoided.

The agitators originally used for mixing the chemicals have been taken out and two new tanks substituted; these are built of quarter-inch boiler steel and are set in masonry. These tanks are each sixteen feet long, eight feet wide, and three feet two inches deep. The bottom is fluted and through each of three valleys runs an iron pipe perforated with quarter-inch holes about fifteen inches apart. These pipes are connected by means of a main, four-inch pipe to an air receiver. Through the holes in these pipes air is blown at a pressure of sixty pounds, although so high pressure is not absolutely necessary and even air taken directly from the compressor has worked satisfactorily. This air agitates the liquid giving it the appearance of boiling.

The lime is thus thoroughly mixed with the water in the tank and runs from it in the form of milk of lime. The old practice of grinding the lime has been abandoned, it having been found that slaking in water was just as efficient and that a more economical use obtained by this thorough water-slaking before coming in contact with the sewage. By these changes a considerable saving in power used has resulted and, by the more thorough slaking of the lime, the amount required has been reduced about thirty per cent.

The treatment originally adopted as recommended by Engineer Allen, consisted in the addition to the sewage of lime and aluminum sulphate. It has been found, however, that the alumina need not be used, on account of the large quantities of iron sulphate contained in the sewage. This iron sulphate is not evenly distributed through the sewage of the day but comes at stated periods. At night, when the sewage is comparatively weak, that containing the copperas is stored crude in one or two of the settling basins and is used during the day, when there is a scarcity of iron and when otherwise aluminum sulphate should be added. By utilizing this iron sulphate, considerable expense is avoided and a perfectly clear, odorless effluent obtained. Lime alone is now added to the sewage, about 900 pounds being required for each million gallons. The highest grade obtainable is used, as it proves most economical in the end. The chemicals formerly entered the sewage just above the salmon ladder but have since been carried about 200 feet up the sewer, that a more thorough mixture might be obtained.

The chemical precipitation of sewage has been practiced in England for more than twenty-five years and yet, the published results of experiments performed there are so meager as to be practically of no assistance here. Consequently when this method was adopted in Worcester great faith had to be placed in future developments. From the first day the plant was operated, continued experiments have been made; at first these were wholly mechanical and random but it was soon found that a systematic study of the whole problem must be made if the work was to be successful. Accordingly the problems met in actual manipulation are made subjects of special investigation

in the well-equipped laboratories. That this move has been productive of good is shown by the reduction of nearly fifty per cent. in the cost of treatment, so far as effected by the chemicals used. Analyses of sewage and effluent are made daily. The samples for analysis are each composed of twenty-four portions taken hourly. Thus by averaging results for several days a mean is obtained, so that comparisons may be made with a certainty that the effluents correspond to the sewages. The percentage of impurity removed from the sewage is readily calculated and is indicative of the efficiency of the plant. Records of the analyses are kept in two forms: one is simply the numerical tabulation, the other a graphic illustration showing at a glance the result of treatment over any period of time. It will be noticed, from accompanying Table A, that the sewage dealt with is remarkably strong, considering that about half of it is water coming directly from North Pond. It is also interesting to note that the effluent contains only two and one-half parts per 100,000 parts matter in suspension and that of this only one and one-tenths parts are organic matter. Thus by treatment the organic suspended matter has been removed to the extent of 90.76 per cent. The total dissolved residue and the total and dissolved fixed residue are negative results, undoubtedly due to the large quantity of lime retained in solution in the effluent. From Table A the result of treatment of sewage since July can be followed by months, and the averages are given for the whole period. The work done as shown by the results of these analyses is very good and should fully carry out the object of the plant; *viz.*, not to transform sewage into a potable water, but to abate and finally terminate a nuisance to neighboring villages along the Blackstone river. During the last three years the sludge has been disposed of in various ways and numerous experiments have been performed and are now being carried on, which for lack of space cannot be described at this time. It may be added that the aim has been to make the plant attractive to the eye by the architecture of the new buildings, the lighting system and the grading around the basins, that the visitor may have his preconceived, erroneous impression of disagreeable sights and odors dispelled.

TABLE A.

Date of Collection.	Residue on evaporation.									Ammonia.				Oxygen Consumed.		Chlorine.
	Total residue.			Volatile residue.			Fixed residue.			Free.	Albuminoid.			Unfiltered.	Filtered.	
	Total.	Dissolved.	Suspended.	Total.	Dissolved.	Suspended.	Total.	Dissolved.	Suspended.		Total.	Dissolved.	Suspended.			
Sewage, July 19–31, 1893	70.2	48.0	22.2	32.1	17.9	14.2	38.1	30.1	8.0	1.043	0.622	0.403	0.219	5.62	3.18	6.64
Effluent, " " " "	59.2	56.0	3.2	16.0	13.5	2.5	43.2	42.5	0.7	0.973	0.356	0.239	0.069	3.29	2.56	6.44
Parts removed	11.0	— 8.0	19.0	16.1	4.4	11.7	— 5.1	—12.4	7.3	0.073	0.266	0.164	0.231	2.33	0.62	0.2
Per cent. "	15.67	—16.67	85.59	50.16	24.59	82.39	13.39	—41.20	91.23	6.71	42.78	40.69	46.58	41.47	19.5	2.99
Sewage, Aug., 1893	61.2	40.9	20.3	30.7	18.6	12.1	30.5	22.3	8.2	1.137	0.558	0.258	0.300	5.9	3.24	6.49
Effluent, " "	53.9	50.7	3.2	14.9	13.5	1.4	39.0	37.2	1.8	1.083	0.333	0.264	0.069	3.7	3.42	6.49
Parts removed	7.3	— 9.8	17.1	15.8	5.1	10.7	— 8.5	—14.9	6.4	0.054	0.225	—0.06	0.231	2.2	— 0.18	0.00
Per cent. "	11.92	—19.33	84.24	51.47	27.42	88.43	27.87	66.82	78.05	4.75	40.33	—2.32	77.00	37.28	— 5.56	0.00
Sewage, Sept., 1893	62.1	43.4	18.7	29.3	17.0	12.3	32.8	26.4	6.4	1.488	0.522	0.247	0.275	5.11	3.15	6.16
Effluent, " "	54.0	51.7	2.3	14.6	13.5	1.1	39.4	38.2	1.2	1.426	0.25	0.204	0.046	3.33	3.03	6.01
Parts removed	8.1	— 8.3	16.4	14.7	3.5	11.2	— 6.6	—11.8	5.2	0.062	0.272	0.043	0.229	1.78	0.12	0.15
Per cent. "	13.04	—19.13	87.70	50.17	20.59	91.05	—20.12	—44.70	81.25	4.17	52.11	17.42	83.28	34.83	3.81	2.43
Sewage, Oct., 1893	67.7	46.4	21.3	28.7	16.6	12.1	39.0	29.8	9.2	1.584	0.576	0.279	0.297	4.96	2.69	5.57
Effluent, " "	54.0	51.6	2.4	13.3	12.5	0.8	40.7	39.1	1.6	1.504	0.288	0.214	0.074	3.37	3.13	6.31
Parts removed	13.7	— 5.2	18.9	15.4	4.1	11.3	— 1.7	— 9.3	7.6	0.08	0.288	0.065	0.223	1.59	— 0.44	— 0.74
Per cent. "	20.21	—11.20	88.74	53.65	24.70	93.40	— 4.36	—31.21	82.60	5.05	50.00	33.3	75.08	32.06	—16.36	—13.3
Sewage, Nov., 1893	57.5	41.7	15.8	22.8	13.1	9.7	34.6	28.6	6.0	1.548	0.45	0.22	0.23	4.49	2.14	5.69
Effluent, " "	51.4	50.0	1.4	12.1	11.5	0.6	39.3	38.5	0.8	1.465	0.196	0.155	0.041	3.49	3.30	5.97
Parts removed	6.1	— 8.3	14.4	10.7	1.6	9.1	— 4.7	— 9.9	5.2	0.83	0.254	0.065	0.189	1.00	— 1.16	— 0.28
Per cent. "	10.69	—19.91	91.11	46.93	12.21	93.80	—13.58	—34.61	86.67	5.36	56.44	29.54	82.19	22.27	—54.2	— 4.92
Av. of sewage analysis, July 19 to Dec. 1, 1893	62.8	43.5	19.3	28.3	16.5	11.8	34.5	27.0	7.5	1.395	0.536	0.266	0.27	5.17	2.85	6.05
" Effluent " " " " " "	53.9	51.5	2.4	13.9	12.8	1.1	40.0	38.7	1.3	1.325	0.276	0.213	0.063	3.43	3.15	6.23
Parts removed	8.9	— 8.0	16.9	14.4	3.7	10.7	— 5.5	—11.7	6.2	0.070	0.26	0.053	0.207	1.74	— 0.3	— 0.18
Per cent. "	14.18	—18.40	87.56	50.88	22.43	90.67	15.94	—43.33	82.6	5.010	48.49	19.88	76.67	33.65	—10.53	— 2.98

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. IV.]

OIL-GAS.[1]

BY W. A. NOYES, W. M. BLINKS AND A. V. H. MORY.[2]

SOME years ago Armstrong and Miller[3] made a study of the gas made from petroleum by subjecting it to a high temperature, and of the oil deposited on condensing the gas. The following study of the gas made from petroleum by a somewhat different process and which gives in some respects different results may be of interest.

In the Pintsch system[4] as described by Armstrong and Miller two **D** shaped retorts of cast iron are set one above the other, the largest size in use being six feet four inches long, ten inches wide and nine and three-fourths inches deep. The retorts are heated to a bright cherry-red and the oil may be run into the upper retort at the rate of about twelve and one-half gallons per hour. About eighty feet of gas per gallon of oil is considered a good yield.

By the Citizens Fuel and Gas Company of Terre Haute, gas is made from petroleum in large generators, one having a capacity of about 450 cubic feet of gas per minute, and two smaller ones with a capacity of 250 feet per minute, during the generation of the gas. The larger generator consists of an outer cylindrical shell of three-eighths-inch boiler steel, twenty feet high by eight feet in diameter, lined with fire-brick to a thickness of sixteen inches. The interior is composed of alternate chambers and checker-work compartments of fire-brick. Starting at the bottom there is an open chamber to the height of two and one-half feet, then, resting upon six twelve-inch arches, the checker-work of brick is built up, rows of brick, touching end to end and two and one-half inches apart, extending from wall to wall, composing the first tier, then upon these other rows are laid at

[1] Read at the Brooklyn meeting, August 15, 1894.

[2] The work described in this paper formed the basis of a thesis presented to the Faculty of the Rose Polytechnic Institute by Mr. W. M. Blinks and Mr. A. V. H. Mory for the degree of Bachelor of Science.

[3] *J. Chem. Soc.*, (London) **49**, 74, (1886).

[4] *J. Soc. Chem. Ind.*, *1884*, 463. We are indebted to Mr. W. B. Landon of Lafayette College for this statement, as the Journal is not accessible to us.

right angles to the first, then the next tier so as to be directly over the open squares formed by the first two rows, and so on, making the checkerwork to the height of five and one-half feet. The bricks are laid in, one upon another, without mortar or fire-clay.

Above this checkerwork is a chamber three feet high, then arches and more checkerwork for five and one-half feet and then another chamber extending to the top. A heavy iron door fourteen inches in diameter is provided at the top. By opening and shutting this it is made to act as a regulator for equalizing pressures when reversing operations. For heating the generator, oil is injected into the top and middle chambers by means of a steam-jet, air being admitted at the same points through five-inch valves. For generating gas, oil is injected into the top chamber through three jets. The gas which is formed leaves the chamber at the bottom through a sixteen-inch pipe lined with fire-brick and leading into the water-seal. The gas as it leaves the generator is too rich for burning in ordinary burners, hence in the seal-box it is diluted with ordinary air injected by steam through a four-inch pipe into the top of the seal. In the process as formerly used this air was injected into the generator with the oil and the oxygen which it contained appeared as carbon dioxide and carbon monoxide in the gas produced. This form of the process is still in use elsewhere.

The seal-box is three and one-half feet in height by four feet in diameter and the pipe leading from the generator dips eight inches below the water surface. A stream of cold water runs continuously into the seal-box, condensing the tar which is carried with the overflow water into the tar well. From the seal the gas passes through a tower scrubber twenty feet in height where it is washed with cold water, then through a tubular condenser, from this through a second scrubber and then through two purifying boxes, $14 \times 14 \times 3$ feet with a twenty-four inch seal. From the purifiers the gas passes through the station meter and thence to the holder. The purifying material used is technically known as Laming's Mass, and is prepared by treating wood shavings with copperas and lime, four barrels of copperas and about the same amount of lime being used to 300 bushels of shavings.

TEMPERATURE.

The destructive distillation of the oil in the process of gas-making is an endothermic operation, large quantities of heat being taken up from the hot brickwork, and the operation can only be carried on for from seven to ten minutes at a time, when the heating must be recommenced and continued for approximately the same length of time.

The temperatures in the generator were measured by noting the melting-points of salts. The salt was wrapped in platinum foil; this was placed in a sheet iron tube attached to an iron rod and the insertion was made through a hole in the side of the generator.

Measurements of the lowest temperature were made by introducing the salts immediately after the gas-making ceased and withdrawing them at the end of two minutes. Sodium chloride was unaltered in all trials at the first temperature, potassium chloride fused in about three minutes, while potassium bromide melted in less than two minutes. The lower temperature is, therefore, between the melting-points of potassium bromide and potassium chloride.

At the highest temperature sodium carbonate fused but calcium fluoride was unaltered. Experiments with sodium sulphate were rejected because the salt was apparently reduced by the gases to which it was subjected.

In assigning a temperature in degrees some difficulty is experienced, as authorities differ as regards the melting-points of these salts. The following values are given by Carnelly,[1] and quoted in the work of Mills and Rowan on fuels, page 341, and by Victor Meyer, and Riddle.[2] The values of the latter, however, are stated as being preliminary only and the melting-point of sodium carbonate especially, is stated, in a later paper, to be too high.

	Carnelly.	Meyer and Riddle.
Potassium bromide	.....	715° C.
Potassium chloride	734° C.	766° C.
Sodium chloride	772° C.	851° C.
Sodium carbonate	814° C.	1098° C.
Calcium fluoride	902° C.	.....

The lower temperature may be stated with some degree of certainty as being about 750° C., while the higher temperature is probably 900° to 1,000° C.

[1] *J. Chem. Soc.*, [London] *1878* and *1880*. [2] *Ber. d. chem. Ges.*, **26**, 2443.

COMPOSITION OF THE GAS.

The following determinations of the technical composition of the gas were made with Orsat's apparatus, the determinations of methane and hydrogen being made by explosion with an excess of air and the addition of oxyhydrogen gas, the large amount of methane rendering an explosion with air alone almost impossible. The illuminants were determined by absorption in fuming sulphuric acid. The first two determinations were duplicated with Hempel's apparatus with almost identical results. The "total carbon" in the gas was determined by exploding a known volume of the gas with an excess of air and determining the volume of carbon dioxide formed. The ethylene and propylene are calculated on the assumption that the illuminants consist exclusively of these two gases. It is well known, of course, and will be further shown below, that this is not the case, but for the purpose of calculating the heat of combustion of the gas the error introduced is slight and is certainly less than on the assumption, usually made, that the illuminants consist entirely of ethylene.

The heat of combustion is calculated on the basis of one cubic foot of the gas at 0° C., burned to carbon dioxide and vapor of water. The following values are used, deduced from the values given in Winkler's "Technische Gasanalyse."

One cubic foot of ethylene		gives	1573.3	English heat units.		
" " "	propylene	"	2324.8	"	"	"
" " "	carbon monoxide	"	342.4	"	"	"
" " "	methane	"	964.3	"	"	"
" " "	hydrogen	"	289.8	"	"	"

	Feb. 20. Undiluted gas. Per cent.	Feb. 20. Diluted gas. Per cent.	May 22. Diluted gas. Per cent.	June 5. Diluted gas. Per cent.
Carbon dioxide	2.3	2.1	0.7	0.8
Illuminants	28.1	19.9	19.3	15.9
Oxygen	0.2	5.9	7.0	7.7
Carbon monoxide	0.6	1.8	0.0	0.0
Methane	44.8	32.3	33.2	36.0
Hydrogen	20.5	14.2	6.9	6.1
Nitrogen	3.5	23.9	32.9	33.5
	100.0	100.0	100.0	100.0
Total carbon—carbon dioxide	115.7	85.6	85.5	77.0
Illuminants { Ethylene	16.2	10.3	6.3	7.5
Illuminants { Propylene	11.9	9.6	13.0	8.4
English heat units per cubic foot	1025.0	744.0	741.0	678.0

The small amount of carbon dioxide and carbon monoxide present in the gas is worthy of especial remark. Steam is used to inject the oil into the generator, but the analyses show that the steam must pass out at the end almost entirely unchanged. It follows from this that in an atmosphere of reducing gases and at a temperature of 700° to 900° C. it is impossible to burn carbon to carbon monoxide or dioxide by means of steam. This is still more apparent in those forms of the process in which air is introduced into the generator. One of us has made many analyses of gases produced in that way and in every case the oxygen of the carbon dioxide and carbon monoxide combined was less than that of the air introduced. These facts have a very important practical bearing as regards the use of steam with petroleum in the manufacture of gas.

The gas directly from the producer contained 1.83 grains of sulphur per cubic foot. The purified gas contained 0.025 grain per cubic foot.

EFFICIENCY.

The amount of oil required for 1,000 cubic feet of gas varies somewhat with the condition of the generators. The following determinations were made:

I. Feb. 20. One run of the large generator when it was about to be shut down for repairs.

Oil per 1,000 cubic feet of diluted gas,	for heating...	2.3 gallons.
" " " " " "	generating	10.7 "
Total.....		13.0 "

II. June 5. Average of five runs of the large generator just fitted with new brickwork.

Oil per 1,000 cubic feet of diluted gas,	for heating...	1.4 gallons.
" " " " " "	generating	9.7 "
Total.....		11.1 "

On comparing the analyses, it will be seen that the gas of June 5 was diluted somewhat more than that of Feb. 22, so that the real difference in efficiency is only about six per cent. As the oil used was different and that of June 5 was, apparently, of better quality, no reliance can be placed on the difference.

So much time was taken for other parts of the work that these

determinations were not repeated so many times as they should have been. Apparently, however, about ten gallons of oil are used in the large generator for generating 1,000 cubic feet of diluted gas and 1.5 to 2.0 gallons of oil are used for heating. When we consider the amount of the dilution, these results are somewhat lower than those reported by Armstrong and Miller. Unfortunately they give no analyses of the gas.

The oil used on Feb. 20 contained some water and an analysis gave

	Per cent.
Carbon	81.0
Hydrogen	12.7

The specific gravity was 0.843.

The oil used on June 5 was nearly free from water and had a specific gravity of 0.865.

We will take the run of June 5 as a basis for calculating, approximately, the efficiency of its plant. If we assume the oil to contain eighty-six per cent. carbon and fourteen per cent. hydrogen one gallon of the oil would give, when burned to vapor of water, about 140,000 English heat units, and the amount of oil required for the manufacture of one cubic foot of gas would give about 1,550 English heat units. Since the gas itself gives 678 units per cubic foot (see analysis), about forty-four per cent. of the heating power of the oil is found in the gas.

Without going into the details of calculation, it may be of interest to state that about thirty-five per cent. of the heating effect of the oil used in heating the generator, is lost by reason of the high temperature of the smoke gases, and an approximately equal amount of heat is carried away by the gas during the generation of the latter. It is probable that at least ten per cent. of the heating effect of the total oil used is lost in this way, though the calculations do not show quite that amount. The remainder of the loss appears to be due mainly to the formation of tar.

PHOTOMETRIC TESTS.[1]

On May 21 a test of the candle-power of the diluted gas, as furnished to consumers, was made, using a Lumner-Brodhun

[1] These tests were made with instruments from the Physical Laboratory, and under the direction of Prof. C. L. Mees.

photometer with a three meter bar. The instrument was made by Hartman and Braun. The Methven slit was used as the direct standard, its value being first determined in terms of a standard amyl acetate lamp which was taken as of one candle-power. A wet meter, which, during one minute, indicated the number of cubic feet burned per hour, was used. Readings were taken on the meter and photometer each minute for five, and sometimes ten, consecutive minutes. Averages of these readings were made and the gas consumption was corrected for temperature.

The first night, tests were made using an argand, a five foot bat-wing, and a small and large Welsbach burner.

The second night, tests were made with a view to determining the relative efficiencies of different sizes of bat-wing burners, and of each size burning under different conditions. The conditions chosen were those of a smooth flame with a consumption rather under the indicated amount, and of a large, forked flame burning as high as possible without blowing. The appended table shows the results obtained,

MAY 22. METHVEN = 2.57 CANDLES.

Burner	Candle power found during the test.	Rate of gas burned per hour during the test.	Candle power corrected for five feet per hour.
Argand	29.3	5.17 cu. ft.	28.4
Five-foot bat wing	33.9	5.27 "	32.2
Small Welsbach	31.4	3.25 "	48.3
Large Welsbach	57.13	6.06 "	47.1

MAY 23. METHVEN = 2.36 CANDLES.

Nature of flame.	Burner.	As above.	As above.	As above.
Smooth	2 ft. bat wing.	14.20	3.21 cu. ft.	22.12
Forked	" "	23.32	5.54 "	21.05
Smooth	3 "	18.53	3.49 "	26.54
Forked	" "	30.02	6.32 "	23.75
Smooth	4 "	19.66	3.43 "	28.66
Forked	" "	37.45	6.74 "	27.78
Smooth	5 "	28.00	4.47 "	31.32
Forked	" "	39.88	6.43 "	31.01
Smooth	6 "	25.01	3.96 "	31.58
Forked	" "	45.01	7.06 "	31.87
Smooth	7 "	29.32	4.43 "	33.10
Forked	" "	53.18	8.27 "	32.15

It will be seen that the larger burners are most efficient and that, with one exception, the smooth flame gives better results. This is especially true of the smaller burners. A sample of the gas taken on May 22 gives for the calculated heating effect 741 English heat units. The statement of the analysis is given elsewhere.

COMPOSITION OF THE ILLUMINANTS.

In order to determine the presence and the amount of benzene and similar hydrocarbons in the gas, these were determined by a modification of the method of Hempel and Dennis, (see next paper), and also by absorption in absolute alcohol and subsequent dilution with salt water. Both methods gave essentially the same result and showed that about 1.2 per cent. by volume of the gas consists of the vapor of these hydrocarbons. From the oil obtained by the second method pure metadinitrobenzene was easily obtained by nitration and crystallization.

To determine the composition of the other gases forming the illuminants, gas directly from the generator was aspirated through an absorption train consisting of two one-liter bottles packed in ice to condense the tar, then two one-half liter bottles half filled with an ammoniacal solution of cuprous chloride to absorb acetylene, next a bottle of the same size half filled with dilute sulphuric acid to absorb ammonia fumes from the cuprous chloride solution, next three Drechsel wash-bottles standing in ice-water, the first two containing one hundred grams each of bromine with about half an inch of water above, and the third containing distilled water for the collection of bromine carried over from the other two, and finally a wash-bottle half full of a solution of sodium hydroxide to absorb bromine fumes. Approximately 125 liters of gas were passed through the train to effect the saturation of the bromine.

The bromine compounds were washed twice with caustic soda, then with distilled water, were separated, dried with calcium chloride, and fractioned. More than one-half came over between 127° and 150°. The residue remaining in the distilling bulb solidified on cooling. It was crystallized from alcohol and from ligroin when it melted at 113°–113.5°. An analysis gave the following results:

0.0750 gram gave 0.1500 gram AgBr.

	Cal. for $C_4H_6Br_4$.	Found.
Br.....	85.56	85.11

Armstrong and Miller[1] obtained a bromide melting at 116°, which they considered to be divinyl tetrabromide (1, 2, 3, 4 tetrabrombutane). The substance described above was probably the same, but less pure, as we have worked with much smaller quantities.

The portion of the bromides boiling from 127° to 150° was redistilled and gave three fractions, the largest 129°–133°, that from 133°–139° next and that from 139°–143° least. After fractioning again, a determination of the molecular weight by the air-displacement method of Victor Meyer, was made with the portion boiling at 130° to 133°. The results agreed fairly with the molecular weight of ethylene bromide. Determinations of the molecular weight of the fraction 140°–143° were unsuccessful owing to decomposition of the bromide. There can be little doubt, however, that the bromides consisted chiefly of ethylene and propylene bromides, the former being present in much larger amount than the latter.

A considerable precipitate was obtained in the ammoniacal solution of cuprous chloride, indicating the presence of appreciable amounts of acetylene and its homologues. In this respect our results differ from those of Armstrong and Miller.

TAR.

The amount and character of the tar varies considerably with the conditions of running. Two samples of the tar were examined, one which was thick and viscous, another which was comparatively thin. No essential difference in qualitative composition was established. The lower boiling substances contained in the tar were separated by distillation with superheated steam, the higher boiling products by direct distillation. In the direct distillation much trouble was experienced from frothing and it was found necessary to heat the tar at first in small quantities in an open dish until the frothing ceased. The residue was then distilled as usual.

Without going into the details of the work the results of the study may be stated briefly as follows:

[1] *J. Chem. Soc.*, (London) **49**, 81, (1886).

Benzene and its lower boiling homologues appear to be present in the tar in only small amount. No positive evidence of their presence was obtained, although it has been shown that benzene is present in the gas.

Naphthalene is present in considerable amount and was identified by melting-point and boiling-point.

Anthracene is also present and was identified by melting-point and by conversion into anthraquinone. An approximate quantitative determination of the amount of anthracene was also made, showing the presence of about 0.35 per cent.

From the portion coming over at about 425° there was obtained, by crystallization, a solid melting at 250° and probably crysene.

From the portion boiling still higher a green crystalline solid melting at about 240° was obtained but not in sufficient amount for its identification.

Attempts to isolate phenol were unsuccessful, though it is probably present in small amount.

The results of the investigation confirm the conclusion of Armstrong and Miller that benzene and allied hydrocarbons may be formed, at high temperatures, from hydrocarbons which bear no simple relation to them.

In conclusion we wish to express to Mr. J. J. Kirkham, Superintendent of the Terre Haute Citizen's Fuel and Gas Company, our thanks for many favors shown us in the course of the work.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. V.]

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.[1]

BY W. A. NOYES AND W. N. BLINKS.

SOME time since Hempel and Dennis[2] described a method of determining benzene vapors in illuminating gas which depends on their absorption in a very small quantity of absolute alcohol. The amount of mercury required and the difficulty of applying the method as described by these authors led us to

[1] Read at the Brooklyn meeting, August 15, 1894.

[2] *Ber. d. chem. Ges.*, **24**, 1162. Also the translation of Hempel's Gas Analysis by L. M. Dennis, p. 221.

9-19-94

attempt the determination with the use of a Bunte burette. The results were so satisfactory that it seems worth while to describe our method of procedure.

One hundred cc. of gas are taken in the burette and measured, either as usual, with a column of water of definite height above, or, perhaps better, with a side tube or bottle attached below so that the gas is brought to atmospheric pressure. The water is then completely removed from the cup of the burette above and the water in the burette is drawn down to the lower stop-cock as usual for the introduction of reagents. Instead of introducing the alcohol from below, however, two or three cc. of absolute alcohol are poured into the cup above and allowed to enter the burette, one cc. at a time. After each admission of the alcohol enough time is given for it to thoroughly run down before more is admitted and care is taken that the walls of the burette are uniformly moistened with the reagent. After withdrawing the alcohol below in the usual manner, two or three cc. of water are admitted above and withdrawn below and then more water is admitted above till the gas is brought to the original pressure, and the volume read.

To test the accuracy of the method, several determinations of the amount of benzene in the gas described in the last paper, were made. This gave 1.2, 1.3, 1.2, 0.5, and 1.2 per cent. The fourth determination was evidently in error for some unknown reason.

Twelve cubic feet of the same gas were passed through a meter, then through two large calcium chloride drying tubes, and then through three Drechsel wash-bottles containing absolute alcohol and a fourth empty bottle to condense vapor carried over, all being surrounded by ice. On dilution with salt-water, 16.8 cc. of liquid hydrocarbons were obtained. Considering these hydrocarbons to consist of benzene they would occupy in the form of vapor at 20° a volume of 4.46 liters. Twelve cubic feet are equal to 340 liters, of which 4.46 liters is 1.31 per cent. When we consider that a portion of the hydrocarbons obtained must have consisted of toluene, naphthalene and other hydrocarbons, whose vapors would occupy a smaller volume than benzene for a given weight, the agreement is satisfactory.

A DEVICE FOR THE ADJUSTMENT OF A BALANCE.[1]

By Frank T. Green.

Received July 27, 1894.

IT is a matter of surprise to intending purchasers that some sensitive balances lack a method of adjustment. I do not allude to the analytical balance only. The assay, prescription, or pulp balance, often has this important improvement wanting. It is well known that the method of adjusting by screws on one or both ends of the beam is satisfactory. Also, that by means of a flag on the top and center of the beam—frequently used by Oertling—a wonderfully close adjustment can be reached.

It is not the intention to criticise these methods, but rather to show how an instrument lacking these improvements can be made adjustable by a person not a mechanic.

By means of a small strip of metal, fashioned after Fig. 1, and

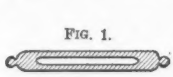


Fig. 1.

Fig. 3.

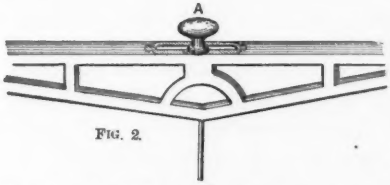


Fig. 2.

preferably made of brass, any balance having a center screw on top of beam A can be made adjustable.

Fig. 1 represents such a device to be fastened to the top of beam in the center in such a manner as to slide either to the right or left as required. When the point of adjustment is reached it can be fixed by tightening the central screw, Fig. 2.

The strip, Fig. 1, or the arrow, Fig. 3, can be made in a few minutes of tinned iron, brass, or sheet proof-silver. The latter metal always being at hand in an assay office. The arrow method being adjusted by turning either to the right or left.

[1] Read at the Midwinter Fair Congress of Chemists, San Francisco, June 8, 1894.

NOTE ON A FORM OF SILVER OBTAINED IN THE REDUCTION OF THE SULPHIDE BY HYDROGEN.[1]

By Francis C. Phillips.

Received July 2, 1894.

IT is a well-known fact that many of the metals are reduced from their oxides, sulphides, and other compounds by hydrogen at high temperatures.

In the majority of such cases the form in which the metal is set free depends upon its fusibility. When both the metal and its compound are fusible only at temperatures far above that at which reduction by hydrogen occurs, the reduced metal usually retains the form originally possessed by its compound, becoming, however, somewhat more porous. Iron reduced by hydrogen from the oxide, sulphide, or chloride, appears as a porous mass or fine powder. The same is true of platinum and of copper.

In the case of other metals, the character of the original compound may exercise a determining influence on the form of the metal after its reduction.

If silver chloride be heated in hydrogen to about 300° C., reduction occurs with formation of hydrogen chloride. The reduced silver appears as a compact, rounded mass, somewhat rough, and having a moderate degree of luster. On heating precipitated silver sulphide in hydrogen, a decomposition occurs with formation of hydrogen sulphide at about the melting-point of silver chloride (450° C.).

The reaction is slow at this temperature, but is more rapid at a somewhat higher heat. The dull, black powder soon begins to assume a slightly lustrous appearance, and at the same time changes gradually into a mass of tangled wires or threads, which lose the black color of the sulphide and exhibit the luster of highly burnished silver. These vary in thickness from that of the finest hairs to that of coarse sewing-thread. They are so linked and knotted together as to be almost inextricable. Under

[1] First printed in Proceedings of Chemical Section, Eng. Soc., W. Pa., April, 1894; communicated by the author.

a microscope it can be readily seen that some of these wires are made up of many smaller ones, which are often imperfectly twisted together, giving the appearance of a rope whose strands had become partly untwisted. Closely-wound coils are often visible. Many of the wires seem to have the smaller ones of which they are composed welded into a single wire, the sides of which then have a fluted or grooved appearance. Owing to the open spaces left in such a mass, a considerable expansion occurs during the reduction. In several trials it was found that the volume of the mass of reduced silver was about three times that of the original sulphide. Experiments made with argentite, the native silver sulphide, using a piece about three cm. thick, led to similar results. The facets of the crystalline mass did not change their shape, nor was their luster much diminished, but a great number of fine wires of lustrous silver seemed to grow out from the mineral in all directions.

Silver sulphide heated in natural gas gave results like those obtained in hydrogen.

Stephanite, Ag_5SbS_4, although fusible in hydrogen with evolution of a little hydrogen sulphide, yielded no silver at a temperature of dull redness.

Copper sulphide, artificially prepared, was slowly reduced by hydrogen at about the melting-point of barium nitrate (600°) with gradual formation of lustrous threads of copper very similar to those obtained in the case of silver.

The observation that silver and copper may be obtained in the form of wires by reduction of the sulphides is not new.

Opificius (*Chemiker Zeitung*, *1888*, 649) announced that such a change occurs.

Bischof (*Annalen der Phys. und Chem.*, *1843*, 289) describes experiments in which silver sulphide heated in steam to the temperature of boiling sulphur was reduced, yielding wire silver, the sulphur of the sulphide at the same time being oxidized to sulphuric acid. Bischof compares this change of crystalline argentite into wire-like forms of metal on reduction to the alteration of augite into asbestos.

Hampe (*Chemiker Zeitung*, *1893*, 1692) has shown that copper in moss-like forms is produced on heating copper sulphide

with filings of the metal to a temperature above the melting-point of copper. The author supposes that copper is dissolved by the fused sulphide and set free again on cooling, being forced out from the fluid interior through the pores of the nearly solid crust in wires or threads. Similar experiments by this author in heating silver with silver sulphide yielded the metal in form of imperfect crystals instead of wires. It is not easy to account for the fact that silver can assume the form of wires or threads so readily on reduction of the sulphide. The fusing-point of silver is 500° higher than the temperature of reduction, and it does not seem possible that the peculiar form of the silver can have been caused by fusion of the metal. Nevertheless, its appearance suggests that it has passed through a liquid or plastic condition. It might seem possible that by the heat of reaction between the silver sulphide and hydrogen silver, at the moment of its reduction, the silver had been heated locally to fusion. The heat of formation of silver sulphide (three calories) is, however, nearly as great as that of hydrogen sulphide 7.2 calories). Hence the heat of reaction could not suffice to fuse the silver. Nor does it seem probable that the quality of ductility of solid silver could be here brought into play, for there is apparently no force which could be supposed to cause a drawing out of the metal. Hampe's explanation, that by being forced out through pores in a solidified and contracting crust, covering a fused interior, copper may have been caused to assume the wire form, cannot apply to silver, for the process here is undoubtedly a gradual one, the sulphide passing without fusion, as reduction occurs, into the form of pure silver wires. The results obtained in laboratory experiments suggest an explanation of one mode of occurrence of native metals in veins.

The wire silver found at Zacatecas, in Mexico, may have originated from reactions of such a character.

Hausmann (*Eng. and Min. Jour.*, May 2, *1890*) describes the occurrence near Breckinridge, Summit County, Colo., of native gold possessing the remarkable wire-like forms, with fluted or grooved surfaces, so characteristic of silver and copper produced in the laboratory by the reduction of the sulphides by hydrogen.

The change into the fibrous condition at the temperature of

the puddling furnace, as cast-iron becomes converted by oxidation into puddled iron, may, perhaps, be considered similar to that which occurs in the reduction of silver sulphide by hydrogen.

The complete removal of impurities from the iron requires a temperature approaching fusion, and the fibers resulting as the metal becomes nearly pure are united into a mass.

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(*Continued from page 643.*)

Another portion of the bean-meal was extracted with a considerable quantity of one per cent. sodium chloride solution; the extract was filtered as clear as possible, and dialyzed in a large vessel containing alcohol. The globulin readily separated after a short time, in well-formed tetrahedral crystals mixed with amorphous matter. This precipitate was filtered off, treated for forty-eight hours with one per cent. sodium chloride solution, filtered clear and again precipitated by dialysis in alcohol, at first quite dilute, but afterwards of gradually increased strength. The substance now separated in large well-formed tetrahedral crystals, the edges of which were slightly curved. This precipitate was filtered off, washed with water, alcohol, and ether, dried and analyzed with results as follows:

PHASEOLIN, PREPARATION 18. CRYSTALS.

	I.	II.	Average.	Ash-free.
Carbon	50.98	....	50.98	52.70
Hydrogen	6.56	....	6.56	6.78
Nitrogen	16.21	16.10	16.16	16.71
Sulphur	0.33	0.29	0.31	0.32
Oxygen	....	....	....	23.49
Ash	3.27	....	3.27	....
				100.00

As dilute acids precipitate proteid substance when added to the sodium chloride extracts of the ground beans, it was thought desirable to make some preparations by this method. Accordingly an extract was prepared by treating the meal with one per cent. sodium chloride solution, and after clearing as completely

as possible by subsidence and decantation, two-tenths per cent. hydrochloric acid was added until a considerable precipitate resulted. After standing some hours the precipitate was filtered off, dissolved in very dilute brine, filtered clear and precipitated by dilution. Only a small part of the substance separated. This preparation, 19, was then washed with water, alcohol and ether, dried and found to contain ash-free, 16.71 per cent. of nitrogen.

The filtrate from 19, when greatly diluted, gave a further precipitate, which, when filtered off and washed with water, alcohol and ether had the following composition:

PHASEOLIN, PREPARATION 20.

		Ash-free.
Carbon	51.85	52.20
Hydrogen	6.91	6.95
Nitrogen	16.15	16.26
Sulphur	0.51	0.51
Oxygen	....	24.08
Ash	0.68	....
		100.00

It is evident that the same globulin was obtained by this method as by those previously followed. Next to be noticed are two preparations of phaseolin, made by diluting the sodium chloride extracts in the manner already described, redissolving the precipitates first obtained in salt solution, and again precipitating by dilution. Preparation 21, contained ash-free 16.65 per cent. of nitrogen.

PHASEOLIN, PREPARATION 22.

	I.	II.	Average.	Ash-free.
Carbon	52.24	....	52.24	52.55
Hydrogen	6.86	....	6.86	6.90
Nitrogen	16.03	16.06	16.05	16.14
Sulphur	0.58	....	0.58	0.58
Oxygen	....	....	....	23.83
Ash	0.58	....	0.58	....
				100.00

The filtrate from 22 was then treated with two-tenths per cent. hydrochloric acid, until a considerable precipitate resulted. This was filtered off, washed with water, alcohol and ether, and analyzed with the following results:

PHASEOLIN, PREPARATION 23.

		Ash-free.
Carbon	51.34	52.12
Hydrogen	6.59	6.70
Nitrogen	15.96	16.21
Sulphur	0.58	0.59
Oxygen	....	24.38
Ash	1.48	....
		100.00

One more preparation of this globulin was made with special reference to its purity. For this purpose a considerable quantity of the globulin was precipitated from a one per cent sodium chloride extract of the beans, and after filtering off, was twice dissolved in dilute sodium chloride solution and precipitated by dilution after filtering clear. The final precipitate was thoroughly washed with water, alcohol and ether and analyzed. When dried over sulphuric acid, the preparation was readily soluble in dilute sodium chloride solution, and consisted entirely of the unaltered phaseolin. Its composition is shown by the analysis of preparation 24.

PHASEOLIN, PREPARATION 24.

	I.	II.	Average.	Ash-free.
Carbon	52.45	52.52	52.49	52.75
Hydrogen	6.99	6.80	6.90	6.95
Nitrogen	16.52	16.39	16.46	16.57
Sulphur	0.56	0.44	0.50	0.50
Oxygen	....	....	....	23.23
Ash	0.69	....	0.69	....
				100.00

The properties of phaseolin as shown by careful examination of preparation 24, dried over sulphuric acid, are as follows:

In cold or warm distilled water it is entirely insoluble.

In sodium chloride solution, and in very dilute acids and alkalies, it is very readily soluble to a clear solution.

Dissolved in ten per cent. sodium chloride solution, it is not precipitated by acetic, hydrochloric, nitric, or sulphuric acids, added in either minute or considerable quantities, although when dilute hydrochloric acid is added to the one per cent. sodium chloride extract of the beans, the phaseolin is precipitated.

Dissolved in large proportion in ten per cent. sodium chloride solution, the proteid is precipitated by adding much pure water.

Solutions of phaseolin in brine are completely precipitated by saturation with ammonium sulphate, but only slightly by saturation with magnesium sulphate or sodium chloride.

Potassium ferrocyanide and acetic acid together, give a precipitate.

With copper sulphate and caustic potash, the usual violet coloration is obtained, and with nitric acid, the xanthoproteic reaction.

Dissolved in ten per cent. sodium chloride solution and heated very slowly in a double water-bath, no turbidity occurs until the temperature is raised to 95°. This turbidity slowly increases as the temperature approaches 100° and after some time, a flocculent precipitate begins to develop, which even after heating for an hour is but slight.

Like other plant-globulins, phaseolin separates from warm concentrated solutions on cooling, and from salt solutions on dialysis, in the form of spheroids.

The striking resemblance in composition of this proteid to the "myosins" found in the seeds of maize and oats, and also to animal myosin, is shown in the following table:

	Phaseolin.	Maize myosin.[1]	Oat myosin.[2]	Animal myosin.[3]
Carbon.....	52.58	52.68	52.34	52.82
Hydrogen.....	6.84	7.02	7.21	7.11
Nitrogen.....	16.48	16.82	16.88	16.77
Sulphur.....	0.56	1.30	0.88	1.27
Oxygen.....	23.54	22.18	22.69	21.93
	100.00	100.00	100.00	100.00

The four proteids, although having many properties in common, as well as a similar composition, are yet characterized by differences so considerable, as to leave no doubt of the individuality of each.

The maize myosin and animal myosin differ from the other two, by their greater content of sulphur, and also in coagulating, the former at 70° and the latter at 55° C.

Phaseolin presents many points of difference from the oat myosin. It is not precipitated from solutions in ten per cent.

[1] *Am. Chem. J.*, 13, 536.

[2] Report Connecticut Agricultural Experiment Station for *1890*, 137-160; also *Am. Chem. J.*, 13, 389; also Report Connecticut Agricultural Experiment Station for *1891*, 135.

[3] Studies from Laboratory of Physiological Chemistry, Yale University, 3, 133

sodium chloride by acids, and but slightly by saturation with sodium chloride, and is thrown down, both by dilution and by dialysis, with much greater difficulty than the oat myosin.

SUMMARY OF ANALYSIS OF PHASEOLIN FROM THE KIDNEY BEAN.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon	52.23	52.60	52.60	....	52.54	....	....	52.72	52.35
Hydrogen	6.95	6.69	6.72	....	6.83	....	....	7.24[1]	6.89
Nitrogen	16.37	16.56	16.17	16.12	16.48	16.23	16.87	16.45	16.52
Sulphur	0.62	0.63	0.63	....	0.58	....	....	0.67	24.24
Oxygen	23.83	23.52	23.88	....	23.57	....	....	22.92	
	100.00	100.00	100.00		100.00			100.00	100.00

	10.	11.	12.	13.	14.	15.	16.	17.	18.[2]
Carbon	52.74	52.49	....	53.06	52.49	52.47	53.22	....	52.70
Hydrogen	6.84	6.80	....	6.85	6.73	6.90	6.86	....	6.78
Nitrogen	16.65	16.85	16.67	16.68	16.45	16.00[1]	16.48	16.29	16.71
Sulphur	0.64	23.86	....	23.41	24.13	24.63	0.48	....	0.32
Oxygen	23.13						22.96	....	23.49
	100.00	100.00		100.00	100.00	100.00	100.00		100.00

	19.	20.	21.	22.	23.	24.	Average.	Ritthausen.
Carbon	....	52.20	....	52.55	52.12	52.75	52.58	52.55
Hydrogen	....	6.95	....	6.90	6.70	6.95	6.84	7.09
Nitrogen	16.71	16.26	16.65	16.14	16.21	16.57	16.48	16.18
Sulphur	....	0.51	....	0.58	0.59	0.50	0.56	0.43
Oxygen	....	24.08	....	23.83	24.38	23.23	23.54	23.75
		100.00		100.00	100.00	100.00	100.00	100.00

PREPARATION OF PHASELIN.

Proteid Remaining in Solution after Separation of the Globulin Just Described.

After precipitating phaseolin by the various methods employed in making the foregoing preparations, the extracts contained proteid matter which could be separated by dialysis in distilled water, by adding acids and by prolonged heating.

These methods of precipitation gave products of nearly uniform composition, except in those cases where the phaseolin had been incompletely separated. Preparations of phaselin were accordingly made as follows:

When a portion of the dialyzed solution from which preparation 1 had been separated, was heated slowly it became turbid

[1] Omitted in making average.

[2] Tetrahedral crystals.

at 40°, flocks appearing at 68° in considerable quantity. When filtered, after heating at 72°, a second turbidity was obtained at 83°, and flocks formed at 87° in greater quantity than at 68°. The remaining solution was dialyzed in alcohol until its volume was reduced by one-half. An equal bulk of strong alcohol was then added to the contents of the dialyzer, and the mixture allowed to stand until the precipitate settled. After three days the solution was decanted and the precipitate washed with absolute alcohol and ether and dried over sulphuric acid. The substance, thus dried, weighed eleven grams. It was finely ground, thoroughly extracted with distilled water, and this extract filtered from the large insoluble residue. The clear solution was then found to become turbid when heated to 63° and to yield a flocculent coagulum at 76°. The entire solution was therefore heated for several hours in a water-bath at 80°, and the coagulum filtered off, washed thoroughly with water, alcohol and ether and dried over sulphuric acid. The 0.9 gram of substance thus obtained, was dried at 110° and analyzed with the following result. Preparation 25.

PHASELIN, PREPARATION 25.

		Ash-free.
Carbon	51.67	51.96
Hydrogen	6.67	6.71
Nitrogen	15.55	15.65
Sulphur } Oxygen }	....	25.70
Ash	0.57	....
		100.00

When the filtrate from 25 was again heated to 80°, a further coagulum resulted. The solution was accordingly kept at this temperature as long as any coagulum was produced, filtered, and the coagulum washed with hot water, alcohol, and ether, and dried for analysis at 110°. This preparation, 26, contained, ash-free, 14.57 per cent. of nitrogen and weighed 0.71 gram.

Two other preparations were made from the filtrate from preparation 3, in nearly the same way as the two last described, the only difference being that the solution was precipitated with alcohol without first concentrating by dialysis in alcohol.

The first coagulum, preparation 27, obtained by heating at

80°, weighed only 0.17 gram, and when dry contained without correction for ash, 14.90 per cent. of nitrogen. The second weighed one gram and had the following composition:

PHASELIN, PREPARATION 28.

		Ash-free.
Carbon	51.19	51.57
Hydrogen	6.87	6.92
Nitrogen	14.36	14.48
Sulphur } Oxygen }	....	27.03
Ash	0.75	....
		100.00

After largely diluting, the filtrate from preparation 16 failed to give any further precipitate on passing carbon dioxide through it for some time. The greater part of this solution was then thrown away, but by chance a little acetic acid was added to the remainder and found to produce a precipitate. This precipitate was filtered off, washed with water, alcohol, and ether, and when dried, weighed 0.27 gram and contained without correction for ash, 14.81 per cent. of nitrogen. Preparation 29.

Another preparation was then made by extracting bean meal with one per cent. brine, diluting the extract with a large quantity of water, and filtering off the precipitate. The filtrate was then treated with two-tenths per cent. hydrochloric acid until a considerable precipitate resulted, which was filtered off and the solution again treated with two-tenths per cent. hydrochloric acid. This final precipitate was filtered off, washed with alcohol and ether and gave one gram of preparation 30, having the following composition:

PHASELIN, PREPARATION 30.

		Ash-free.
Carbon	50.18	51.38
Hydrogen	6.53	6.71
Nitrogen	14.44	14.84
Sulphur } Oxygen }	....	26.87
Ash	2.74	....
		100.00

Again, the filtrate from preparation 10, was treated with an equal volume of strong alcohol and allowed to stand over night.

The next morning, the precipitate which had separated was filtered off and treated with water. This dissolved some of the substance. This solution, filtered clear, when heated, gave a flocculent coagulum at 80°. With acetic, hydrochloric, or nitric acid, it gave a precipitate when the reagents were added in sufficient quantity. These precipitates were soluble in sodium chloride solution, and those produced by hydrochloric and nitric acids, were soluble in an excess of the acid, but that given by acetic acid, was not noticeably soluble in an excess. The precipitate obtained with nitric acid, did not dissolve upon warming, as is the case with such precipitates yielded by proteoses. The reaction of the extract was slightly acid, but it was not possible to precipitate anything therefrom, by the most careful neutralization. The whole solution was then treated with two-tenths per cent. hydrochloric acid; the precipitate thus formed had the following composition:

PHASELIN, PREPARATION 31.

		Ash-free.
Carbon	49.91	51.98
Hydrogen	6.55	6.82
Nitrogen	13.95	14.53
Sulphur } Oxygen }	....	26.68
Ash	4.00	....
	100.00	

The precipitate from which 31 was derived, after this extraction with water, was but slightly soluble in sodium chloride solution, and was therefore treated with two-tenths per cent. potash water. The resulting solution was filtered clear, and hydrochloric acid cautiously added, until a precipitate formed which was collected on a filter and treated in the usual manner. When dry, this preparation, 32, weighed 3.3 grams.

The filtrate from 32 was further treated with two-tenths per cent. hydrochloric acid, and a second precipitate obtained which weighed 0.6 gram; preparation 33.

PHASELIN, PREPARATION 32.

	I.	II.	Average.	Ash-free.
Carbon	51.74	51.74	51.74	52.65
Hydrogen	7.04	7.00	7.02	7.14
Nitrogen	14.89	....	14.89	15.15

	I.	II.	Average.	Ash-free.
Sulphur } Oxygen }	....	....	....	25.06
Ash	1.78	....	1.78	....
				100.00

PHASELIN, PREPARATION 33.

		Ash-free.
Nitrogen	14.24	14.85
Ash	4.12	....

Another preparation was made by extracting 100 grams of bean meal, with 100 cc. of one per cent. sodium chloride solution, and washing the insoluble residue with 100 cc. of the same solution, applied in successive portions. The entire extract was then filtered nearly clear, and dialyzed in alcohol. The alcohol of the outer vessel was frequently renewed, and the process was continued until practically all the proteid matter had separated. The precipitate was then filtered off and extracted with one per cent. sodium chloride solution. Much of the substance remained undissolved. The solution was filtered clear and dialyzed again in alcohol of 0.85 sp. gr. which was renewed once during the process. The precipitate resulting was filtered off and washed with dilute alcohol, absolute alcohol and ether and dried at 110°. Its composition was as follows:

PHASELIN, PREPARATION 34.

		Ash-free.
Carbon	46.49	51.38
Hydrogen	6.25	6.91
Nitrogen	13.27	14.67
Sulphur } Oxygen }	....	27.04
Ash	9.53	....
		100.00

In order to obtain a purer preparation of the proteid by this method, 200 grams of bean meal, first extracted with petroleum-benzine, were treated with one liter of one per cent. sodium chloride solution and after squeezing out, the residue was mixed with another liter of the same solution and again squeezed. After standing over night, the turbid extract was decanted and dialyzed in alcohol for three days, the alcohol being once renewed. This treatment precipitated nearly all the proteids, which were

collected on a filter, and after the solution had run off, the precipitate was suspended in one-quarter per cent. sodium chloride solution, filtered off and washed with the same solution. The clear filtrate and washings were then dialyzed into alcohol until a considerable precipitate had formed which was filtered off and washed successively with fifty per cent. alcohol, stronger alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It was then almost wholly soluble in water, but after drying at 110° it became insoluble, and was washed with water, alcohol, and ether, and again dried, 35.

PHASELIN, PREPARATION 35.

	I.	II.	Average.	Ash-free.
Carbon	49.01	....	49.01	51.37
Hydrogen	6.77	....	6.77	7.10
Nitrogen	14.26	13.82	14.04	14.71
Sulphur } Oxygen }	....	....	....	26.82
Ash	4.58	....	4.58	....
				100.00

[TO BE CONTINUED.]

THE DETERMINATION OF ALBUMEN IN COW'S MILK.

BY L. L. VAN SLYKE.

Received August 22, 1894.

IN Vol. **15**, No. 11 of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, the writer presented a paper on the determination of casein in cow's milk. It is now desired to present another paper supplementary to that and relating to the determination of albumen in cow's milk.

Ordinarily, when we speak of milk albumen, we mean the portion of nitrogen compounds not coagulated by rennet, acid, etc. In other words, we apply the term albumen to the nitrogen compounds left after removing the casein proper. This use of the term albumen is inaccurate, because, after removing from normal milk its casein, there remain, at least, two nitrogen compounds or classes of nitrogen compounds. One of these is coagulated by heat, especially in the presence of dilute acids, while the other is not coagulated under these conditions. To the former only of these two, the term albumen is properly applicable.

DETAILS OF METHOD.

The filtrate obtained, after separating the casein by the method described in the article above referred to, is placed in a water-bath heated to the boiling temperature of water, the beaker containing the filtrate being covered with a watch-glass crystal. The solution is kept at this temperature until the albumen coagulates and settles to the bottom, leaving the supernatant liquid clear. Ten or fifteen minutes usually suffices to accomplish this. The precipitate is filtered, washed and then treated according to the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by the factor 6.25 gives the amount of albumen.

It was thought that too long boiling of the albumen precipitate might cause some of it to redissolve; and, in order to ascertain what effect the length of time of heating influenced the results, the digestion was varied from five minutes to ten hours. The tabulated results are as follows:

	Length of time solution containing albumen was heated.									
	5 Minutes.	10 Minutes.	15 Minutes.	20 Minutes.	30 Minutes.	45 Minutes.	1 Hr.	2 Hrs.	4 Hrs.	10 Hrs.
No. of sample of milk.	Per cent. of nitrogen in albumen contained in milk.									
1..... *a*	....	0.060	....	0.057	0.054	0.056	0.057	0.061	0.046	0.060
"..... *b*	....	0.062	0.058	0.048	0.051	0.063	0.062	0.059	0.055	0.054
"..... Average	....	0.061	0.058	0.053	0.053	0.059	0.059	0.060	0.051	0.057
2..... *a*	0.014	0.054	0.054	0.052	0.052	0.051	0.052	0.047	0.045	....
"..... *b*	0.044	0.053	....	0.054	0.051	....	0.051	0.051	0.049	....
"..... Average	0.029	0.053	0.054	0.053	0.052	0.051	0.051	0.049	0.047	....
3..... *a*	0.054	0.053	0.049	0.052	0.051	0.053	0.057	0.057	0.056	0.058
"..... *b*	0.054	0.047	0.053	0.056	....	0.057	0.057	0.060	0.053	0.055
"..... Average	0.054	0.050	0.051	0.054	0.051	0.055	0.057	0.058	0.055	0.056
4..... *a*	0.057	0.064	0.061	0.061	0.065	0.065	0.062	0.062	0.069	0.065
"..... *b*	0.062	0.055	0.065	0.063	0.064	0.062	0.065	0.066	....	0.065
"..... Average	0.059	0.060	0.063	0.062	0.064	0.063	0.063	0.064	0.069	0.065
Average of all results	0.047	0.056	0.056	0.055	0.055	0.057	0.057	0.058	0.056	0.059

An examination of the foregoing table shows:

(1) In one case, heating for five minutes gave low results; in two other cases, good results.

(2) In general, the results varied little with increased length of time of heating.

(3) There was a slight tendency to higher results with

increased length of heating, but such increase was more or less irregular and, at most, amounted to only 0.002 or 0.003 per cent. of nitrogen.

(4) It would, therefore, appear that entirely satisfactory results can be obtained by heating the solution containing albumen under the given conditions for ten or fifteen minutes, while an increased length of time of heating does not practically change the results.

It may be stated that the precipitate formed always filters readily and washes easily.

SEPARATION AND DETERMINATION OF THE NITROGEN COMPOUNDS OF COW'S MILK.

Below we give a brief summary of our method as we employ it in effecting the determination and separation of the three classes of nitrogen compounds present in the normal milk of cows.

1. Total Nitrogen Compounds.—Determine the amount of total nitrogen by the Kjeldahl method and multiply by the factor 6.25.

2. Casein.—Weigh out about ten grams of milk, dilute in a beaker with about ninety cc. of water at 40°–42° C., and add at once 1.5 cc. of a solution containing ten per cent. of acetic acid, by weight. Stir with a glass rod and let stand three to five minutes longer. Then decant on a filter, wash two or three times with cold water by decantation and then transfer precipitate completely to filter. Wash once or twice on filter. The washed precipitate and filter paper are then digested as in the regular Kjeldahl method for the determination of nitrogen, and the determination completed in the usual manner. To calculate the nitrogen into an equivalent amount of casein, multiply the amount of nitrogen by the factor 6.25.

3. Albumen.—The filtrate obtained above in separating casein is placed in a water-bath and heated to the boiling temperature of water for ten or fifteen minutes. The filtered and washed precipitate is then treated by the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by 6.25 gives the amount of albumen.

4. Remaining Nitrogen Compounds.—The remaining compound or compounds of nitrogen are determined by difference,

subtracting from the amount of total nitrogen compounds the sum of the casein and albumen.

In conclusion, I wish to call attention to the crude nomenclature in common use in stating the results of milk analysis for nitrogen compounds. It is an almost universal custom to call the total nitrogen compounds of milk casein. It would be quite as correct to call the fat of milk palmitin or some similar name. This wrong use of the term casein leads to much confusion, and it is highly desirable that we should use a more discriminating nomenclature. It is also desirable that, in making analysis of milk, pains should be taken to separate and determine the different kinds of nitrogen compounds, since our knowledge of these compounds is far from complete.

I am much indebted to Mr. A. L. Knisely for assistance rendered by him in carrying out the analytical details of the work.

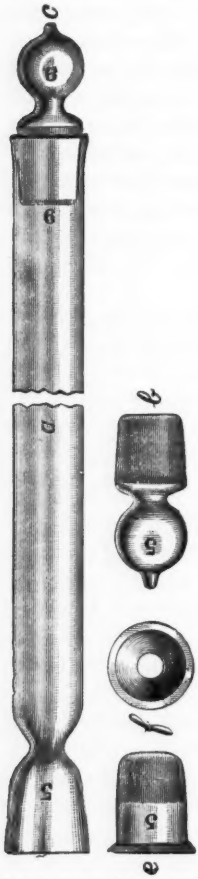
AN APPARATUS ("LYSIMETER") FOR DETERMINING SOLUBILITIES.

By Charles Rice.

Received July 11, 1894.

IN determining the solubility of a substance in some liquid at a given temperature, there is usually but little difficulty encountered when the solvent is not very volatile and the temperature at which the determination is to be made is not high. With a highly volatile solvent, and a high temperature, however, certain difficulties present themselves which are liable to lead to error. The main difficulty is encountered in the endeavor to separate from the original solution, which usually contains an excess of the substance in suspension, a *filtered* portion at the same temperature as that of the solution. The higher this temperature is, the more difficult becomes the removal of a portion without the introduction of errors by the ordinary methods of filtration. It appears, therefore, that it is only necessary to modify the method of filtration in such a way as to maintain the temperature of the original solution unchanged in order to eliminate these errors. This may be easily accomplished by upward filtration into a tube placed in the original solution, and so constructed that it will enable the operator to control the act of filtration, as well as accurately to determine the amount of solvent

and dissolved material. For this purpose the little apparatus here described has been found very serviceable.



The apparatus consists of a glass tube *a*, fifteen cm. long and one cm. in external diameter, provided at one end with a well-ground stopper *c*, while the other end is cup-shaped, there being a contracted neck between the cup and the main tube. Into this cup is made to fit, a carefully ground glass bell *e*, having a perforation in its bottom (as shown in *f*). There is also a stopper *b* which is carefully ground to fit into the cup, and which is inserted after the glass bell *e* has been removed. The several stoppers, etc., are all numbered to show where they belong.

To show how the apparatus is used it will be best to quote a practical example.

Let us assume that the solubility of morphine in boiling alcohol is to be determined. It will be necessary to provide for such an amount of liquid that at least one-half of the glass tube *a* may be immersed in the liquid. In the case of comparatively cheap solvents and substances to be dissolved, beaker glasses may be used; for more expensive materials, test-tubes of such a size that there will be no great waste of material are preferable.

The glass tube is made ready by inserting the stopper *c*, and introducing into the cup-shaped end the glass bell *e*, containing a pellet of purified cotton and prevented from dropping out by a thin platinum wire fastened around the contracted neck and crossed over the mouth of the bell. A sufficient amount of alcohol having been introduced into a beaker, or test-tube, heat is applied and morphine added until, after the boiling has been kept up some time, a portion of the alkaloid remains

undissolved. The prepared glass tube is now inserted in the liquid. As long as the stopper *c* closes the mouth of the tube no liquid will be able to filter upwards. When the tube has acquired the temperature of the boiling liquid the stopper *c* is removed, whereupon the liquid will begin to filter through the pellet of cotton and rise in the tube as far as the quantity of liquid will permit. In order to insure perfect uniformity of the liquid within and without the tube, it is best to allow the filtered portion to flow back through the pellet of cotton once or several times. The stopper *c* having then been inserted, the tube is withdrawn, turned upside down, the glass bell removed, and the stopper b inserted. The tube is now carefully cleaned with alcohol, and laid aside until cold. Its tare having previously been determined, the increase in weight represents the weight of the solution contained therein. On transferring or washing the contents into a tared beaker or capsule and evaporating, the weight of the dissolved morphine will be found.

The apparatus here described, which has been frequently in use during several years, and to which, for brevity's sake, the name *lysimeter* (from the Greek *lysis*, solution) has been given, was made for the writer in a very satisfactory manner by Mr. Emil Greiner, of New York City.

NEW YORK, July 7, 1894.

NEW BOOKS.

THE DECOMPOSITION OF THE FIXED ALKALIES AND ALKALINE EARTHS. By Humphry Davy, 1807–1808. Alembic Club Reprint, No. 6. 12 mo. 51 pp. Edinburgh: William F. Clay. 1894.

This number of the Alembic Club Reprints contains the Bakerian Lecture delivered by Davy before the Royal Society in 1807, and also part of a paper communicated by him to the same Society in the following year. The Bakerian Lecture is on the Decomposition of the Fixed Alkalies and on the General Nature of the Alkaline Bodies. The other paper is on the Decomposition of the Earths, with observations on the metals obtained from the alkaline earths.

In the first paper we have the first published record of the experiments by which Davy proved the compound nature of the alkalies and prepared the metals potassium and sodium. The

second paper contains a description of similar experiments upon the earths and alkaline earths, only that part which deals with the successful experiments being reprinted. W. R. O.

THE DISCOVERY OF OXYGEN. By Joseph Priestley, 1775, and Carl Wilhelm Scheele, 1777. Being Nos. 7 and 8 of Alembic Club Reprints. Edinburgh: William F. Clay. 1894.

Among the first things learned by students in chemistry, is that "oxygen was discovered almost simultaneously by Priestley in England, in 1774, and Scheele, in Sweden, in 1775." That the work of these men was independent of each other is also well known. Many have become acquainted with their work in a general way, but few have had the opportunity of following the original experiments as described by the experimenters. This opportunity is offered now by the publishers of the Alembic Club Reprints. Nos. 7 and 8 of this series are the Discovery of Oxygen. Part I (No. 7) by Joseph Priestley, and Part II (No. 8) by Carl Wilhelm Scheele, the latter a translation. They consist of sections taken from larger works of these authors, and, save for a short preface by the publisher, are without note or comment. Both Priestley and Scheele are minute in the description of the numerous experiments carried out in this work.

They began experimenting at different ends of the subject. Priestley was of the "try something" type of worker, and in his different experiments the peculiarities of "dephlogisticated air," as he afterwards called it, "obtruded themselves upon him." He first obtained the "air" then studied its properties. He tried to obtain this "air" from every available substance. The bulk of it was obtained from mercuric oxide and red lead and nitric acid. Scheele, on the other hand, found that air was not a simple substance, but contained a gas, which he called "fire air." The experiments which were performed when this truth was discovered are well described. They consisted in placing oxidizable substances in bottles which were well corked, and allowing the air in them to act for different periods of time, then opening the bottles under water and noting the diminution in the volume of air by the water entering the bottles. Then the work of producing "fire air" was undertaken, numerous experiments were carried out, the results of which are well known.

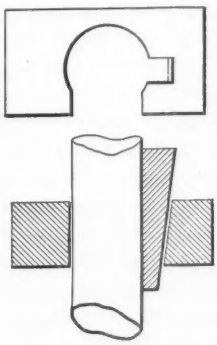
These two men had the theory of combustion in their grasp, and almost explain it in their writings, that they were unconscious of this fact is surprising.

The publishers of these Reprints are to be thanked for placing before the chemical world the work of these two men in such a handy and attractive form. A digest of a work is good, but the original furnishes the only true satisfaction. So these little books should be extremely valuable to the student, by enabling him to see the discovery of oxygen in its original shape.

OWEN L. SHINN.

NOTES.

Convenient Burette Clamp.—A convenient form of burette holder may be made from the appended sketch. A simple wedge being employed in place of the screw clamp to hold the tube in position. The surface of the wedge bearing on the tube should be slightly curved to ensure accurate contact. Cork is not necessary on bearing parts, as very slight pressure on upper end of wedge causes the tube to be held with great rigidity. Holder should be made of maple, wedge of hickory or other hard wood.—*Clarence Quinan.*



A New Atmospheric Element.—Lord Rayleigh and Professor Ramsay announce the discovery of a supposed new element contained in the atmosphere to the extent of about one per cent. Two methods of separation have been used. The first method consists in passing high tension electrical sparks through a mixture of equal bulks of air and oxygen confined over potash solution until no further diminution in volume ensues. The excess of oxygen is then absorbed by alkaline pyrogallate. The second method consists in removing the oxygen from air by red hot copper and the nitrogen by heated magnesium. The remaining gas has a sp. gr. of 18.9 and is more inert than nitrogen.

Wm. Crookes has examined the spectrum of the gas when the

induction spark is passed through a tube containing the new gas under an exhaustion of eight mm., and finds that "the spectrum is a very definite and characteristic one, and the lines differ in position from those of nitrogen. The appearance more resembles a metallic spectrum, and no flutings similar to those of nitrogen are to be seen." Professor Dewar suggests that the new element may be an allotropic form of nitrogen analogous to red phosphorus, and that the processes of preparation may be really methods of manufacture. E. H.

The Post-Mortem Detection and Estimation of Strychnine—Allerton S. Cushman. (*Transactions of the Academy of Science of St. Louis*, **6**, 537.)

The author recommends the following method for the detection and estimation of strychnine in toxical cases: The mass to be examined is comminuted and digested over night at a warm temperature with water acidulated with acetic acid, filtered through muslin and then through paper, the solution evaporated, an excess of eighty per cent. alcohol added, boiled, filtered, and extraction repeated. The liquid is then evaporated, the residue taken up with water and a little acetic acid, and the solution shaken repeatedly with acetic ether, as long as anything is extracted—twelve extractions may be necessary. A volume of acetic ether equal to that of the solution is now added, and sodium carbonate to alkaline reaction. After shaking, the acetic ether is separated and the extraction repeated. The strychnine is usually moderately pure as obtained by the evaporation of the acetic ether, but for quantitative estimation it is dissolved in dilute acetic acid, filtered, the solution extracted with ether-chloroform (1:1), ammonia added, and the extraction with ether-chloroform repeated twice. The residue obtained by evaporating the ether-chloroform is nearly pure and is weighed. Two experiments with known amounts of strychnine mixed with considerable amounts of meat, sugar, starch, and water, and allowed to stand in a warm place for two weeks, gave a recovery of about eighty-seven per cent. of the strychnine present. Directions for chemical, crystallographic, and physiological tests are given. Two toxical cases in which the method was applied are also given. W. A. Noyes.